Designing P-type bi-stable overcrowded alkene-based chiroptical Photoswitches

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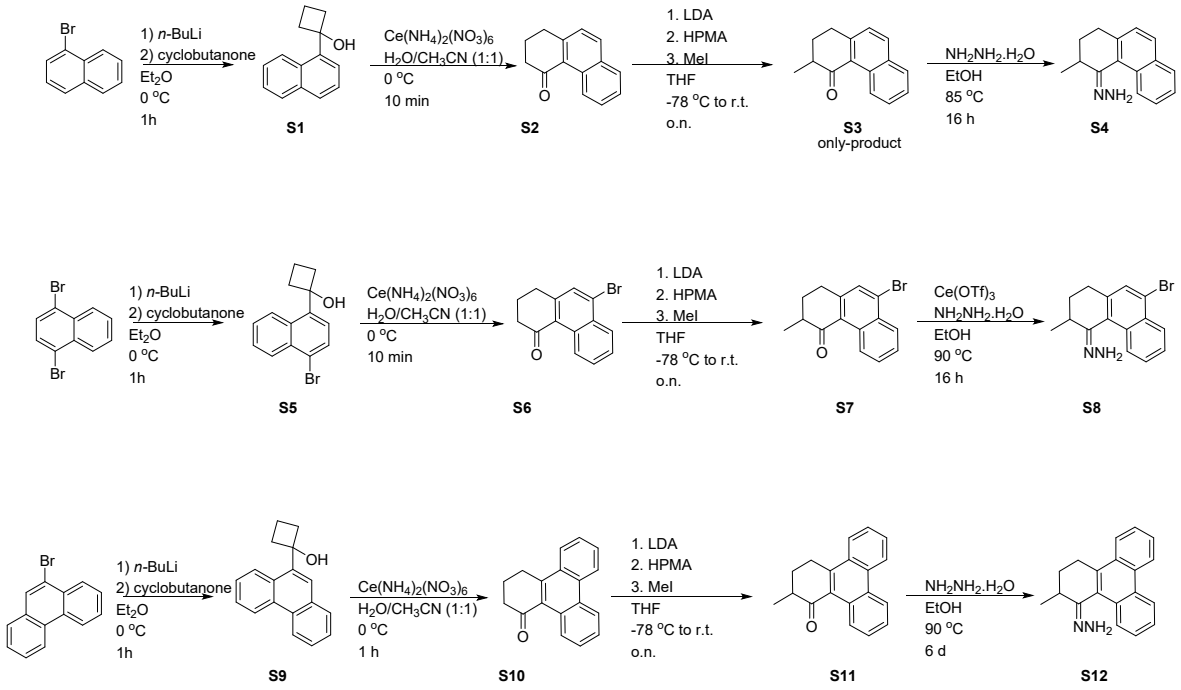
General Information

All reagents were obtained from commercial sources such as Aldrich, TCI, Fluorochem, combi-Blocks and used as received. Anhydrous dichloromethane (DCM), THF, Diethyl ether was obtained from a solvent purification system (MBRAUN SPS systems, MBSPS-800). Flash column chromatography was performed using silica gel (SiO_2) purchased from Merck (type 9385, 230-400 mesh) or on a Büchi Reveleris purification system with Büchi cartridges. NMR spectra were recorded on Varian AMX400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) and Varian Unity Plus (^{1}H: 500 MHz, ^{13}C: 125 MHz) spectrometers. Chemical shifts are denoted in parts per million (ppm) relative to the residual solvent signal (for $CDCl_3$ δ 7.26 for 1H, δ 77.16 for ^{13}C and for CD_2Cl_2 δ 5.32 for ^{1}H, δ 53.84 for ^{13}C or DMSO--d_6 2.50 for ^{1}H, δ 39.52 for ^{13}C. For ^{1}H NMR spectroscopy, the splitting pattern of peaks is designated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), ddd (doublet of doublets of doublets), ddt (doublet of doublets of triplets) or dddd (doublet of doublets of doublets of doublets). High resolution mass spectrometry (ESI or APCI-MS) was performed on a LTQ Orbitrap XL spectrometer with ESI ionization. UV/Vis absorption spectra were measured on a Hewlett-Packard 8453 diode array spectrometer in a 1 cm quartz cuvette. The UV/Vis setup used to measure the quantum yields of isomerization is described elsewhere.[1] The UV/Vis and NMR irradiation experiments were performed using fiber-coupled LEDs (M365F1, M455F1) obtained from Thorlabs Inc. All UV/Vis experiments are performed directly using the solvents from the solvent purification system without degassing. The irradiation studies by ^{1}H NMR analysis were performed using CD_2Cl_2 or THF-d_8 treated with K_2CO_3 without degassing. Enantiomers of switch **1** were separated by HPLC (Chiralcel-ODH, eluent: heptane/isopropyl alcohol = 99.7/0.3).[2] We followed the photoisomerization of switches by UV/Vis or ^{1}H NMR (*ex-situ* irradiaton) spectroscopy until no further changes were observed in the spectra, that is at least two consecutive spectra recorded were the same, which confirms that the PSS has been reached. We also note that the irradiation time of samples in NMR or UV/Vis relevant concentration regime is vastly different and much longer irradiation times are needed to reach PSS for the NMR samples.

Experimental Procedures

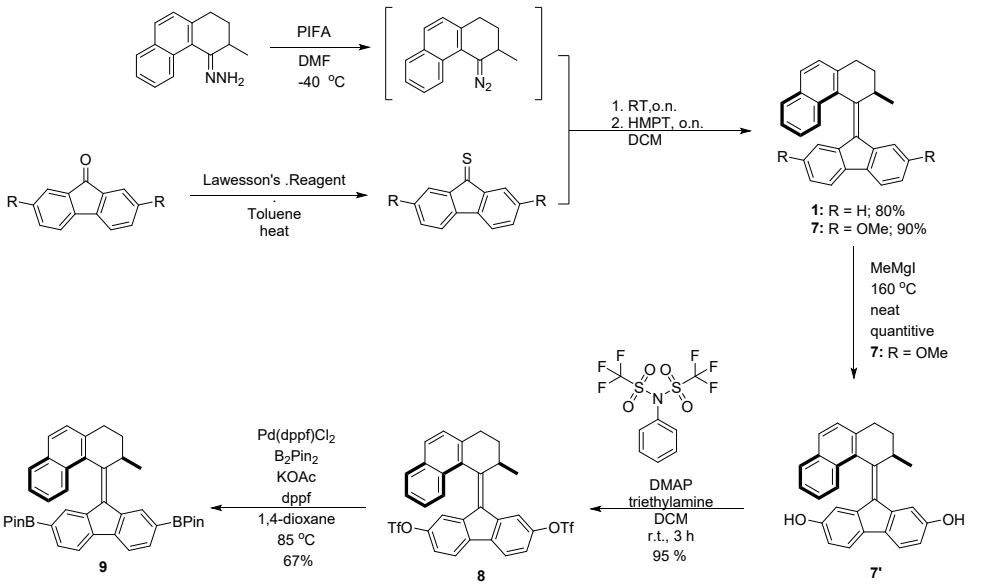
Synthesis of Top-parts



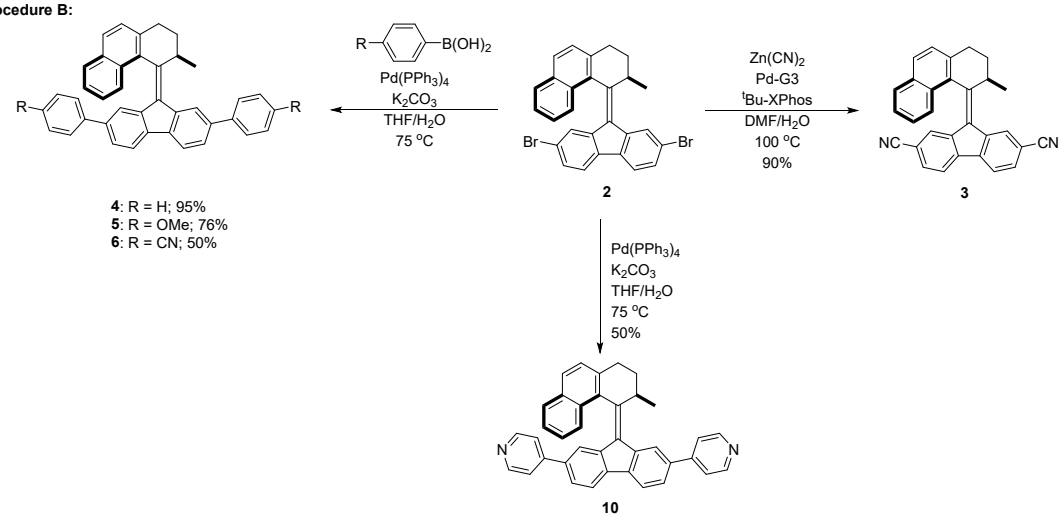
Scheme S1. Synthesis of top-parts.

Synthesis of Switches

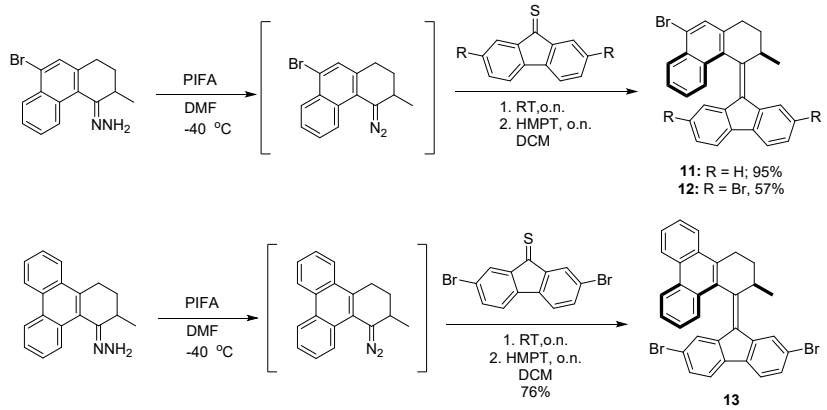
Procedure A:



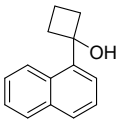
Procedure B:



Br-substituted derivatives



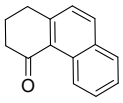
Scheme S2. Synthetic route for synthesis of switches **1**-**10** and Br-substituted derivatives.



1-(Naphthalen-1-yl)cyclobutan-1-ol. Compound **S1** was prepared following a modified version of a previously reported procedure.[3] Under a N_2 atmosphere, 1-bromonaphthalene(10.4 g, 50 mmol) was dissolved in dry ether (150 ml), the solution was cooled to 0 °C and *n*-butyllithium (33 mL, 52.5 mmol) was added dropwise via a syringe. The yellow solution was stirred at 0 °C for 1 h and then cyclobutanone (4.3 mL, 55 mmol) was added in one portion and the resulting mixture was stirred for 1 h upon which a precipitate was formed. The suspension was quenched by aq. NH_4Cl (sat.) and extracted with ether, washed with water, brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by crystallization from pentane to afford the alcohol ***S*1** as a white solid (9.40 g, 47.5 mmol, 95%). Analytical data in agreement with the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.27 (m, 1H), 7.90 – 7.86 (m, 1H), 7.80 (dt, *J* = 8.2, 1.1 Hz, 1H), 7.54 – 7.48 (m, 3H), 7.44 (dd, *J* = 8.2, 7.1 Hz, 1H), 2.90 – 2.82 (m, 2H), 2.67 – 2.59 (m, 2H), 2.25 (s, 1H), 2.16 (dddd, *J* = 11.0, 9.2, 5.5, 3.4 Hz, 1H), 1.71 (tdd, *J* = 8.8, 4.4, 2.3 Hz, 1H).

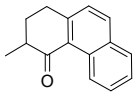
^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 134.9, 130.9, 129.1, 128.9, 126.4, 125.9, 125.8, 125.0, 123.0, 78.7, 36.9, 14.6.



2,3-Dihydrophenanthren-4(1*H*)-one. A solution of ***S*1** (3.96 g, 20.0 mmol), in a water-acetonitrile mixture (50 mL: 50 mL) was stirred in an open round-bottom flask at 0 °C for 10 min. Subsequently, $Ce(NH_4)_2(NO_3)_6$ (27.5 g, 50.0 mmol) was added and the mixture was stirred at 0 ℃ for 10 min. Then, the reaction was quenched by addition of aqueous saturated sodium thiosulfate solution (100 mL). The mixture was extracted with ethyl acetate (3×50 mL) and the combined organic layers were washed with water, brine, dried over Na_2SO_4, filtrated and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 20:1) to afford ***S*2** as a colorless solid (2.00 g, 10.2 mmol, 51%). Analytical data in agreement with the literature.[3]

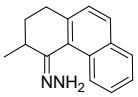
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.81 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.63 (ddd, *J* = 8.6, 6.8, 1.5 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 3.13 (t, *J* = 6.1 Hz, 2H), 2.79 (dd, *J* = 7.3, 6.0 Hz, 2H), 2.20 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 146.9, 134.4, 132.9, 131.5, 129.0, 128.4, 127.5, 127.1, 126.8, 126.0, 41.2, 31.8, 23.2.

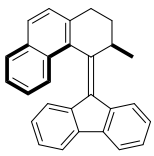


3-Methyl-2,3-dihydrophenanthren-4(1*H*)-one. Under N_2 atmosphere, to a solution of di*iso*propylamine (2.00 mL, 15.5 mmol) in THF (20 mL) cooled to 0 °C, was added dropwise, *n*-butyllithium (1.6M in hexane, 8.40 mL, 13.4 mmol) and the mixture stirred for 2 h. After cooling to -78 °C, hexamethylphosphoramide (HMPA, 7.50 mL) was added, and the reaction mixture was stirred for 1 h. A solution of ***S*2** (2.90 g, 10.5 mmol) in THF (10 mL) was added dropwise, and the mixture was stirred at -78 ℃ for 2 h. After addition of iodomethane (1.00 mL, 15.6 mmol) at -78 °C, the mixture was stirred overnight to room temperature. The reaction was quenched with aqueous NH_4Cl, and the mixture was extracted with ethyl acetate. The organic layer was washed with aqueous $NaHCO_3$, water, and brine, dried with anhydrous Na_2SO_4, filtrated and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane:CH_2Cl_2 =3:1) to afford ***S*3** as a white solid product (2.20 g, 7.70 mmol, 74%). Analytical data in according to the literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33 (dd, *J* = 8.8, 1.3 Hz, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.82 – 7.75 (m, 1H), 7.59 (ddd, *J* = 8.6, 6.8, 1.5 Hz, 1H), 7.46 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 3.25 – 3.06 (m, 2H), 2.75 (dqd, *J* = 13.5, 6.8, 4.6 Hz, 1H), 2.26 (dq, *J* = 13.5, 4.6 Hz, 1H), 1.96 (dddd, *J* = 13.1, 11.8, 10.7, 5.1 Hz, 1H), 1.31 (d, *J* = 6.8 Hz, 3H).



(*Z*/*E*)-(3-Methyl-2,3-dihydrophenanthren-4(1*H*)-ylidene)hydrazine. The compound was synthesized following the procedure previously reported.[4] Ketone ***S*3** (0.86 g, 3.00 mmol) was added to a solution of ethanol and $NH_2NH_2{\cdot}H_2O$ (20 ml + 20 mL) and the mixture was heated under reflux at 85 °C for 16 h. The mixture was extracted with ethyl acetate and washed with water, brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 3:1) to afford ***S*4** as a white solid (420 mg, 1.40 mmol, 46%). Analytical data in agreement with the literature.[4]

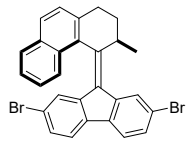


4-(9*H*-Fluoren-9-ylidene)-3-methyl-1,2,3,4-tetrahydrophenanthrene. Lawesson's reagent (282 mg, 0.700 mmol) and 9*H*-fluoren-9-one (180 mg, 1.00 mmol) were added to a vial under a N_2 atmosphere. Dry toluene (10 mL) was added and the reaction mixture was heated at 90 °C for 2 h. After cooling to RT, the reaction mixture was directly poured onto a column and the residue was purified by quick column chromatography (SiO_2, pentane:CH_2Cl_2 = 5:1). Thioketone fraction was collected and concentrated under reduced pressure to yield a dark green solid (to prevent hydrolysis, the product was kept wet with CH_2Cl_2 and was used immediately in the next step). In another two-neck flask under a N_2 atmosphere, hydrazone (67.2 mg, 0.300 mmol) was dissolved in DMF (4 mL). The solution was cooled to −40 ℃ and bis(trifluoroacethoxy)iodobenzene (133 mg, 0.310 mmol) in DMF (3 mL) was added to the stirred solution. The mixture was stirred for 3 min while the color turned from yellow to pink, indicative of the *in situ* formation of the diazo compound. A solution of the 9*H*-fluoren-9-thione (180 mg, 1 mmol) in dry CH_2Cl_2 (5 mL) was added to the mixture. The mixture was allowed to warm to room temperature and stirred for 4 h. HMPT (Tris(dimethylamino)phosphine) (0.3 mL) was then added and stirred for another 24 h. The mixture was diluted with ethyl acetate and washed with water, brine, dried over Na_2SO_4, filtrated and concentrated *in vacuo.* The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 20:1) to afford **1** as pale yellow solid (85.0 mg, 0.240 mmol, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 6.0, 2.9 Hz, 1H), 7.95 – 7.85 (m, 3H), 7.85 – 7.79 (m, 1H), 7.67 – 7.63 (m, 1H), 7.49 – 7.34 (m, 4H), 7.21 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.06 (td, *J* = 7.4, 1.0 Hz, 1H), 6.55 (td, *J* = 7.6, 1.2 Hz, 1H), 5.96 (d, *J* = 8.0 Hz, 1H), 4.34 (h, *J* = 7.0 Hz, 1H), 2.77 (ddd, *J* = 14.1, 4.6, 2.8 Hz, 1H), 2.59 (td, *J* = 13.4, 5.2 Hz, 1H), 2.47 (dddd, *J* = 13.2, 8.2, 5.2, 2.8 Hz, 1H), 1.28 (d, *J* = 6.9 Hz, 3H), 1.23 – 1.13 (m, 1H).

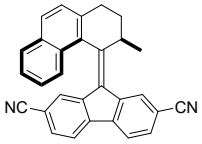
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 141.0, 139.9, 139.6, 138.2, 138.0, 133.7, 133.6, 132.4, 132.2, 128.8, 128.4, 127.5, 127.1, 126.9, 126.9, 126.6, 125.9, 125.4, 125.2, 125.1, 124.8, 119.8, 118.9, 34.9, 31.0, 29.8, 21.1.

HRMS (ESI pos) calcd $C_{30}H_{23}$ $[M+H]^+$: 359.1794, found 359.1795.



4-(2,7-Dibromo-9*H*-fluoren-9-ylidene)-3-methyl-1,2,3,4-tetrahydrophenanthrene. Compound **2** was prepared by following the procedure previously reported.[5] Analytical data in agreement with the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.7 Hz, 1H), 7.92 (dd, *J* = 12.3, 8.1 Hz, 2H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.50 - 7.37 (m, 3H), 7.26 - 7.21 (m, 1H), 7.17 (dd, *J* = 8.1, 1.8 Hz, 1H), 5.96 (d, *J* = 1.7 Hz, 1H), 4.20 (p, *J* = 7.2 Hz, 1H), 2.86 - 2.75 (m, 1H), 2.64 - 2.43 (m, 2H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.25 - 1.17 (m, 1H).

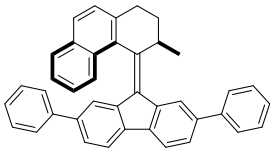


9-(3-Methyl-2,3-dihydrophenanthren-4(1*H*)-ylidene)-9H-fluorene-2,7-dicarbonitrile. Under a N_2 atmosphere, compound **2** (77.0 mg, 150 µmol), $Zn(CN)_2$ (21.0 mg, 180 µmol), *t*-BuXPhos-Pd-G3 (12 mg, 15.0 µmol) and *t*-BuXPhos (17.2 mg, 40.0 µmol) were dissolved in degassed DMF/H_2O mixture (10 mL of DMF, 0.1 mL of H_2O) and the mixture was heated at 100 °C for 3 h. Subsequently, the mixture was poured into water (100 mL), and extracted by ethyl acetate (3x10 mL). The organic layer was washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 2:1) to afford **3** as pale yellow solid (55.0 mg, 135 µmol, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.3 Hz, 1H), 7.96 (ddd, *J* = 12.7, 11.2, 8.4 Hz, 3H), 7.81 – 7.73 (m, 2H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.45 – 7.37 (m, 2H), 7.22 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 6.19 (dd, *J* = 1.3, 0.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 1H), 2.86 (dt, *J* = 14.4, 3.7 Hz, 1H), 2.65 – 2.47 (m, 2H), 1.34 (d, *J* = 7.0 Hz, 3H), 1.30 – 1.25 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 142.5, 141.1, 140.7, 138.8, 138.7, 132.5, 131.7, 131.5, 131.2, 130.7, 130.5, 130.3, 129.1, 129.0, 128.8, 127.6, 126.1, 125.7, 124.0, 121.3, 120.5, 119.7, 119.0, 111.9, 111.2, 35.7, 30.3, 29.6, 20.9.

HRMS (ESI pos) calcd $C_{30}H_{20}N_2$ $[M]^+$: 408.1621, found 408.1617.

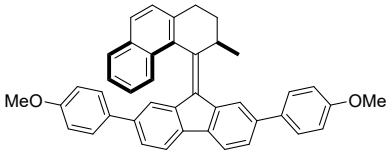


4-(2,7-Diphenyl-9*H*-fluoren-9-ylidene)-3-methyl-1,2,3,4-tetrahydrophenanthrene. Under a N_2 atmosphere, compound **2** (26.0 mg, 50.0 µmoll), phenylboronic acid (25.0 mg, 200 µmol), tetrakis(triphenylphosphine)palladium (5.80 mg, 5.00 µmol) and K_2CO_3 (69.0 mg, 500 µmol) were mixed in THF (3 mL) and H_2O (3 mL), and reacted at 75 °C for 24 h. Then the mixture was poured into water (10 mL) and extracted with ethyl acetate (3x10 mL). The organic layer was washed with water, brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 25:1) to afford **4** as pale yellow solid (24.0 mg, 25.0 µmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.01 (dd, *J* = 14.9, 8.4 Hz, 2H), 7.90 (dd, *J* = 8.1, 3.3 Hz, 2H), 7.78 – 7.65 (m, 4H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.49 – 7.38 (m, 3H), 7.36 – 7.26 (m, 2H), 7.18 – 7.11 (m, 3H), 6.62 – 6.53 (m, 2H), 6.23 (d, *J* = 1.6 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 1H), 2.76 (dt, *J* = 14.0, 3.8 Hz, 1H), 2.64 – 2.45 (m, 2H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.23 (dd, *J* = 7.0, 4.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 142.2, 141.3, 140.5, 140.3, 139.9, 139.3, 139.1, 138.7, 138.4, 133.5, 133.3, 132.6, 132.3, 129.1, 129.0, 128.8, 128.3, 128.3, 127.4, 127.4, 127.3, 127.1, 126.9, 126.8, 126.7, 126.2, 125.9, 125.5, 125.3, 124.6, 124.6, 120.1, 119.2, 35.1, 31.1, 29.9, 21.0.

HRMS (ESI pos) calcd $C_{40}H_{31}$ $[M+H]^+$: 512.2454, found 512.2450



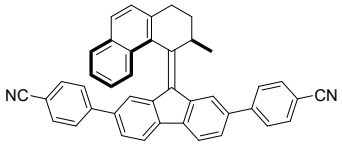
4-(2,7-Bis(4-methoxyphenyl)-9*H*-fluoren-9-ylidene)-3-methyl-1,2,3,4-tetrahydrophenanthrene. Under a N_2 atmosphere, compound **2** (26.0 mg, 50.0 µmol), 4-cyanophenylboronic acid (31.0 mg, 200 µmol), tetrakis(triphenylphosphine)palladium (7.00 mg, 6 µmol), K_2CO_3 (69.0 mg, 500 µmoll)

were dissolved in THF (3 mL) and H_2O (3 mL), and the mixture reacted at 75 °C for 16h. Then the mixture was poured into water (10 mL) and extracted by ethyl acetate (3x10 mL). The organic layer was washed with water, brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 1:4) to afford **5** as pale yellow solid (22.0 mg, 39.0 µmol, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 – 8.27 (m, 1H), 8.01 (dd, *J* = 15.6, 8.4 Hz, 2H), 7.87 (dd, *J* = 22.5, 8.1 Hz, 2H), 7.72 – 7.58 (m, 4H), 7.48 – 7.40 (m, 2H), 7.31 – 7.26 (m, 2H), 7.11 – 7.03 (m, 2H), 6.72 – 6.63 (m, 2H), 6.53 – 6.45 (m, 2H), 4.42 (h, *J* = 7.0 Hz, 1H), 3.90 (s, 3H), 3.78 (s, 3H), 2.75 (ddd, *J* = 14.0, 4.3, 2.7 Hz, 1H), 2.64 – 2.41 (m, 2H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.28 – 1.19 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 158.8, 144.8, 140.5, 139.8, 139.5, 139.1, 138.8, 138.6, 138.0, 134.8, 134.0, 133.6, 133.5, 132.6, 132.3, 128.8, 128.4, 128.3, 127.8, 127.1, 126.5, 126.2, 125.6, 125.4, 125.3, 124.2, 120.0, 119.0, 114.6, 113.8, 55.6, 55.4, 35.1, 31.1, 29.9, 21.0.

HRMS (ESI pos) calcd $C_{42}H_{35}O_2$ $[M+H]^+$: 572.2665, found 572.2643.

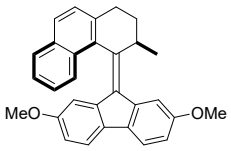


4,4'-(9-(3-Methyl-2,3-dihydrophenanthren-4(1*H*)-ylidene)-9*H*-fluorene-2,7-diyl)dibenzonitrile. Under a N_2 atmosphere, compound **2** (26.0 mg, 50 µmol), phenylboronic acid (30.4 mg, 0.2 mmol), tetrakis(triphenylphosphine)palladium (5.80 mg, 5 µmol), K_2CO_3 (69 mg, 0.5 mmol) were dissolved in THF (3 mL) and H_2O (3 mL), and the mixture reacted under 75 °C for 24h. Then the mixture was poured into water (10 mL) and extracted by ethyl acetate (3*10 mL). The organic layer was washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane:CH_2Cl_2 = 1:1) to afford **6** as pale yellow solid (14.0 mg, 25.0 µmol, 50%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.39 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.97 (t, *J* = 8.8 Hz, 3H), 7.91 – 7.81 (m, 4H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.48 (dd, *J* = 15.1, 8.0 Hz, 4H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 2H), 6.19 (s, 1H), 4.42 (q, *J* = 7.2 Hz, 1H), 2.81 (d, *J* = 15.4 Hz, 1H), 2.56 (ddt, *J* = 18.7, 12.9, 6.0 Hz, 2H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.26 (h, *J* = 6.6, 6.0 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 149.2, 148.8, 148.1, 143.6, 142.9, 141.9, 141.6, 141.4, 141.1, 140.0, 135.6, 135.4, 135.1, 135.1, 134.7, 131.5, 130.9, 130.4, 129.6, 129.4, 128.8, 128.4, 127.9, 127.7, 127.1, 127.0, 123.1, 122.2, 121.5, 121.5, 113.5, 112.9, 37.8, 33.4, 32.3, 23.2. (2 additional aromatic carbon signals are overlapping in the spectrum).

HRMS (ESI pos) calcd $C_{42}H_{32}N_3$ $[M+NH_4]^+$: 578.2591, found 578.2583.

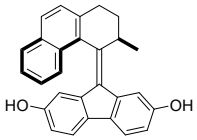


4-(2,7-Dimethoxy-9*H*-fluoren-9-ylidene)-3-methyl-1,2,3,4-tetrahydrophenanthrene. Lawesson's reagent (4.00 g, 10.0 mmol) and 2,7-dimethoxy-9*H*-fluoren-9-one (1.34 g, 5.60 mmol) were added to a vial under a N_2 atmosphere. Dry toluene (20 mL) was added, and the reaction mixture was heated at 80 °C for 2 h. After cooling, the reaction mixture was directly poured onto a column and the residue was purified by quick column chromatography (SiO_2, pentane:CH_2Cl_2 = 2:1). The thioketone fraction was collected and concentrated under reduced pressure to yield a dark purple solid (to prevent hydrolysis, the product was kept wet with CH_2Cl_2 and was used immediately in the next step). In two-neck flask under a N_2 atmosphere, hydrazone (672 mg, 3.00 mmol) was dissolved in DMF (20 mL). The solution was cooled to −40 °C and bis(trifluoroacethoxy)iodobenzene (1.29 g, 3.00 mmol) was added to the stirred solution. Next, the mixture was stirred for 3 min while the color turned from yellow to pink, indicative of the formation *in situ* of the diazo compound. A solution of the thioketone in dry CH_2Cl_2 (20 mL) was added to the mixture. The mixture was allowed to warm to room temperature and stirred overnight. HMPT (Tris(dimethylamino)phosphine) (2.0 mL) was then added and the mixture was stirred for another 24 h. The mixture was diluted with ethyl acetate (10 mL) and washed with water, brine, dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 20:1) to afford **7** as yellow solid (1.13 g, 2.7 mmol, 90%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.93 (d, *J* = 8.6 Hz, 1H), 7.89 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 2.3 Hz, 1H), 7.57 (d, *J* = 8.3 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.22 (m, 1H), 6.94 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.56 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.41 (d, *J* = 2.4 Hz, 1H), 4.28 (p, *J* = 7.2 Hz, 1H), 3.93 (s, 3H), 2.86 (s, 3H), 2.83 – 2.74 (m, 1H), 2.61 – 2.44 (m, 2H), 1.29 (d, *J* = 6.9 Hz, 3H), 1.17 (tdd, *J* = 12.5, 8.7, 4.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 158.0, 144.6, 140.3, 139.4, 139.1, 134.6, 133.5, 133.4, 132.9, 132.4, 132.3, 128.5, 128.2, 127.1, 126.1, 125.4, 125.2, 119.3, 118.8, 115.2, 112.7, 112.25, 109.02, 55.9, 54.5, 34.8, 31.2, 29.9, 20.9.

HRMS (APCI pos) calcd $C_{30}H_{27}O_2$ $[M+H]^+$: 419.2006, found 419.2019.

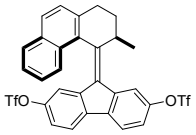


9-(3-Methyl-2,3-dihydrophenanthren-4(1*H*)-ylidene)-9*H*-fluorene-2,7-diol. Under a N_2 atmosphere, a capped vial was charged with **7** (404 mg, 1.00 mmol). MeMgI (3.0 mL, 6.0 mmol, (2 M in Et_2O)) was added and the mixture was stirred until the dissolution of **7**. Subsequently, the temperature was increased to 80 °C to remove the Et_2O in the flow of N_2. After removal of the volatile solvent the temperature was increased again to 160 °C and the reaction mixture was stirred at this temperature until the residue solidified (approximately for 2 h). Next, the vial was cooled down to 0 °C and the reaction mixture was quenched with aq. NH_4Cl (sat.). The residue was dissolved in ethyl acetate (10 mL) and washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The solid **7'** was obtained without further purification (390 mg, 1.00 mmol, quantitative).

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.40 (s, 1H), 8.61 (s, 1H), 7.97 (dd, *J* = 12.0, 8.2 Hz, 2H), 7.79 – 7.72 (m, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.39 (ddd, *J* = 8.1, 6.7, 1.2 Hz, 1H), 7.34 – 7.22 (m, 2H), 6.77 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.43 (dd, *J* = 8.1, 2.2 Hz, 1H), 5.24 (d, *J* = 2.1 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 1H), 2.84 – 2.72 (m, 1H), 2.47 – 2.38 (m, 2H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.07 – 0.98 (m, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 156.0, 155.0, 143.2, 139.2, 138.6, 138.4, 133.1, 132.9, 132.4, 131.9, 131.4, 131.3, 128.7, 128.4, 126.7, 125.8, 124.9, 124.1, 119.3, 118.4, 114.5, 114.2, 112.5, 111.7, 33.9, 30.4, 28.9, 20.7.

HRMS (ESI pos) calcd $C_{28}H_{23}O_2$ $[M+H]^+$: 391.1648, found 391.1642.



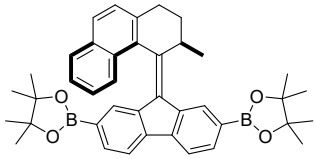
9-(3-Methyl-2,3-dihydrophenanthren-4(1*H*)-ylidene)-9*H*-fluorene-2,7-diyl bis(trifluoromethanesulfonate). Under a N_2 atmosphere, to a two-neck round -bottom flask was charged with DMAP (4-Dimethylaminopyridine) (25.0 mg, 0.200 mmol), diol **7'** (390 mg, 1.00 mmol), *N*-Phenyl-bis(trifluoromethanesulfonimide) (786 mg, 2.20 mmol) and 20 mL of dry DCM was added, followed by trimethylamine (1.00 mL, 6.00 mmol). The progress of the reaction was followed by TLC (pentane: ethyl acetate = 20:1) until no starting material was left (approximately for 3 h). Then the mixture was diluted with CH_2Cl_2 (50 mL) and washed with water, brine, dried over Na_2SO_4, filtrated, and concentrated in *vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 20:1) to afford **8** as yellow solid (621 mg, 0.950 mmol, 95%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.01 (d, *J* = 2.2 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.91 (t, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.40 (ddd, *J* = 8.4, 6.8, 4.4 Hz, 2H), 7.25 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 7.04 (dd, *J* = 8.4, 2.3 Hz, 1H), 5.81 (d, *J* = 2.3 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 1H), 2.61 – 2.47 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.21 (ddt, *J* = 18.3, 12.8, 7.0 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 151.0, 149.7, 149.2, 141.2, 140.4, 140.2, 139.2, 138.0, 132.9, 132.1, 132.0, 131.4, 130.5, 129.0, 127.8, 126.2, 125.8, 124.3, 121.5, 121.0, 120.8, 120.6 (q, J = 69.3 Hz), 120.6, 118.8, 117.7, 117.4 (q, J = 67.9 Hz), 35.8, 30.7, 29.9, 20.7.(For resonances characteristic of $^{13}CF_3$ groups, only two central lines could be observed.)

^{19}F NMR (376 MHz, CD_2Cl_2) δ -72.99, -73.64.

HRMS (ESI neg) calcd $C_{30}H_{19}F_6O_6S_2$ $[M-H]^-$: 653.0517, found 653.0533.

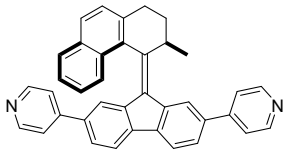


(*R*)-2,2'-(9-(3-Methyl-2,3-dihydrophenanthren-4(1*H*)-ylidene)-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane). Under a N_2 atmosphere, compound **8** (830 mg, 1.27 mmol), B_2Pin_2 (1.94 g, 7.60 mmol), $Pd(dppf)Cl_2$ (100 mg, 0.13 mmol), dppf (87 mg, 0.13 mmol) and KOAc (1.25 g, 12.7 mmol) were dissolved in degassed dioxane (30 mL), and the mixture was heated at 85 °C for 48 h. Then the mixture was concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 4:1) to afford **9** as pale yellow solid (519 mg, 0.85 mmol, 67%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.56 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.78 (m, 4H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.11 (m, 1H), 6.28 (s, 1H), 4.40 (h, *J* = 7.1 Hz, 1H), 2.81 (dt, *J* = 14.4, 3.4 Hz, 1H), 2.68 – 2.48 (m, 2H), 1.40 (d, *J* = 4.5 Hz, 12H), 1.37 (d, *J* = 6.7 Hz, 3H), 1.27 (dd, *J* = 6.9, 4.7 Hz, 1H), 1.13 (s, 6H), 1.08 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 145.5, 143.4, 142.0, 140.5, 138.3, 137.8, 134.2, 133.9, 133.2, 133.1, 132.9, 132.9, 132.2, 131.9, 128.9, 128.7, 126.8, 126.1, 125.2, 125.1, 119.7, 118.8, 84.3, 83.6, 53.8, 35.3, 31.5, 30.1, 25.3, 25.3, 25.0, 24.4, 20.9.

HRMS (ESI pos) calcd $C_{40}H_{45}B_2O_2$ $[M+H]^+$: 611.3499, found 611.3502.

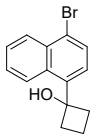


4,4'-(9-(3-Methyl-2,3-dihydrophenanthren-4(1*H*)-ylidene)-9*H*-fluorene-2,7-diyl)dipyridine. Under a N_2 atmosphere, compound **2** (26 mg, 0.05 mmol), pyridine-4-boronic acid (24.6 mg, 0.200 mmol), Tetrakis(triphenylphosphine)palladium (5.8 mg, 5.00 µmol), K_2CO_3 (69.0 mg, 0.500 mmol) was dissolved in THF (3 mL) and H_2O (3 mL), and the mixture was stirred at 75 °C for 24 h. Then the mixture was poured into water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The organic layer was washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 1:1) to afford **10** as yellow solid (14.0 mg, 25.0 µmol, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 2H), 8.46 – 8.27 (m, 3H), 8.08 – 7.91 (m, 4H), 7.80 – 7.70 (m, 2H), 7.70 – 7.62 (m, 2H), 7.47 (td, *J* = 8.2, 1.8 Hz, 2H), 7.38 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.29 (ddd, *J* = 8.3, 6.7, 1.3 Hz, 1H), 6.49 (d, *J* = 5.7 Hz, 2H), 6.26 (d, *J* = 1.6 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 1H), 2.86 – 2.74 (m, 1H), 2.65 – 2.48 (m, 2H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.31 – 1.25 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6, 149.7, 149.1, 148.5, 146.6, 140.9, 140.8, 139.5, 139.4, 138.9, 137.6, 136.5, 133.1, 132.6, 132.6, 132.2, 129.2, 128.5, 127.3, 126.7, 126.3, 125.8, 125.50, 125.23, 124.4, 124.3, 121.8, 121.2, 120.8, 119.8, 35.4, 30.9, 29.9, 21.0.

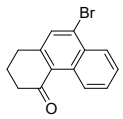
HRMS (ESI pos) calcd $C_{38}H_{29}N_2$ $[M+H]^+$: 513.2325, found 513.2319.



1-(4-Bromonaphthalen-1-yl)cyclobutan-1-ol. Under a N_2 atmosphere, 1,4-dibromonaphthalene (17.2 g, 60.0 mmol) was dissolved in ether (200 ml), the solution was cooled to 0 °C and *n*-butyllithium (39.3 mL, 63.0 mmol) was slowly added *via* syringe to the solution. The yellow solution was stirred under 0 °C for 1 h and then cyclobutanone (5.10 mL, 77.6 mmol) was added and stirred for 1 h, upon which a precipitate was formed. The suspension was quenched by aqueous NH_4Cl (sat.) and extracted with ether washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by crystallization in pentane to afford the alcohol as pale white solid (13.6 g, 49.2 mmol, 82%). Analytical data in according to the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 – 8.27 (m, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.58 (dddd, *J* = 18.6, 8.5, 6.9, 1.3 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 1H), 2.86 – 2.76 (m, 2H), 2.67 – 2.56 (m, 2H), 2.23 – 2.10 (m, 2H), 1.70 (dtt, *J* = 11.1, 8.7, 6.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 133.0, 132.3, 129.0, 128.2, 127.18, 126.9, 126.7, 123.5, 123.5, 78.4, 37.0, 14.7.

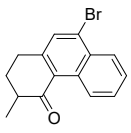


9-Bromo-2,3-dihydrophenanthren-4(1*H*)-one. Compound **S6** was prepared following a reported procedure [3] with few modifications. A solution of **S5** (5.50 g, 20.0 mmol), in a water-acetonitrile mixture (50 mL: 50 mL) was stirred in an open round-bottom flask at 0 °C for 2 min. Subsequently, $Ce(NH_4)_2(NO_3)_6$ (27.4 g, 50.0 mmol) was added and the mixture was stirred at 0 °C for 10 min. Then, saturated aqueous sodium thiosulfate (100 mL) was added to quench the reaction. The reaction mixture was extracted with ethyl acetate (50 mL × 3), the combined organic layers were washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 20:1) to afford white solid product (3.20 g, 11.6 mmol, 58%). Analytical data in according to the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (d, *J* = 8.7 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.59 (t, *J* = 7.7 Hz, 1H), 3.10 (t, *J* = 6.1 Hz, 2H), 2.81 – 2.76 (m, 2H), 2.19 (p, *J* = 6.4 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 146.7, 132.7, 131.4, 131.2, 129.9, 129.6, 127.6, 127.3, 127.2, 127.2, 41.2, 31.4, 22.9.

HRMS (APCI pos) calcd $C_{14}H_{12}BrO$ $[M+H]^+$: 275.0066, found 275.0094.

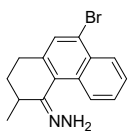


9-Bromo-3-methyl-2,3-dihydrophenanthren-4(1*H*)-one. Under N_2 atmosphere, to a solution of di*iso*propylamine (2.00 mL, 15.5 mmol) in THF (20 mL) cooled to 0 °C atmosphere, was added dropwise *n*-butyllithium (1.6 M in hexane, 8.40 mL, 13.4 mmol) and the mixture was stirred for 2 h. Next, the reaction mixture was cooled to -78 °C, hexamethylphosphoramide (HMPA, 7.5 mL) was added, and stirred for 2 h. Next, a solution of **S6** (2.9 g, 10.5 mmol) in THF (10 mL) was added dropwise, and the mixture was stirred at -78 °C for 2 h. Subsequently, iodomethane (1.0 mL, 15.6 mmol) was added at -78 °C and the mixture was stirred overnight. The mixture was allowed to slowly warm up to room temperature. The reaction was quenched with aqueous NH_4Cl, and the mixture was extracted with ethyl acetate (20 mL × 3). The organic layer was washed with aqueous $NaHCO_3$, water, and brine, dried with anhydrous Na_2SO_4, filtered, and concentrated in *vacuo*. The crude product was purified by column chromatography (SiO_2, pentane:CH_2Cl_2 =3:1) to afford white solid product **S7** (2.20 g, 7.70 mmol, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (dd, *J* = 8.8, 1.3 Hz, 1H), 8.26 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.69 – 7.61 (m, 2H), 7.58 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 1H), 3.24 – 3.03 (m, 2H), 2.76 (tt, *J* = 11.5, 6.7 Hz, 1H), 2.26 (dq, *J* = 13.5, 4.6 Hz, 1H), 1.96 (dtd, *J* = 13.1, 11.3, 5.0 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 145.8, 132.6, 131.3, 131.1, 129.6, 129.4, 127.5, 127.36, 127.2, 127.0, 44.0, 31.1, 30.2, 16.0.

HRMS (APCI pos) calcd $C_{14}H_{12}BrO$ $[M+H]^+$: 289.0223, found 289.0225.



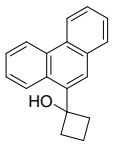
9-Bromo-3-methyl-2,3-dihydrophenanthren-4(1*H*)-ylidene hydrazine. Ketone **S7** (0.860 g, 3.00 mmol) and $Ce(OTf)_3$ (1.90 g, 3.20 mmol) was suspended in EtOH and $NH_2NH_2{\cdot}H_2O$ (20 ml + 20 mL) and the mixture was stirred

under reflux at 85 °C for 16 h. The mixture was extracted with ethyl acetate (10 mL × 3) and washed with water, brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 3:1) to afford white solid **S8** (0.420 g, 1.40 mmol, 46%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 – 8.66 (m, 1H), 8.25 – 8.19 (m, 1H), 7.59 (s, 1H), 7.54 (m, *J* = 5.6 Hz, 2H), 4.61 (s, 2H), 3.21 (dt, *J* = 8.7, 6.7 Hz, 1H), 2.76 (dt, *J* = 15.4, 4.4 Hz, 1H), 2.62 (ddd, *J* = 15.5, 11.5, 4.1 Hz, 1H), 2.28 (dq, *J* = 11.1, 5.0 Hz, 1H), 1.42 (tdd, *J* = 12.6, 8.9, 4.0 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 4H).

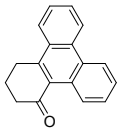
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 139.9, 132.3, 131.7, 130.1, 127.5, 127.4, 126.8, 126.6, 31.4, 30.2, 29.2, 16.2.(one of the aromatic carbon was overlapping).

HRMS (APCI pos) calcd $C_{15}H_{16}BrN_2$ $[M+H]^+$: 303.0491, found 303.0499.



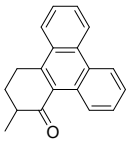
1-(Phenanthren-9-yl)cyclobutan-1-ol. Under N_2 atmosphere, 1,4-dibromonaphthalene(14.8 g, 58 mmol) was dissolved in diethyl ether (200 ml), the solution was cooled to 0 °C, and *n*-butyllithium (38.0 mL, 53 mmol) was slowly added via syringe to this solution. The yellow solution was stirred at 0 °C for 1 h and then cyclobutanone (4.90 mL, 74.6 mmol) was added and stirring was continued for 1 h upon which a solid precipitated. The suspension was quenched by aq. NH_4Cl (sat.) and extracted with ether (200 ml) and washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by crystallization in pentane to afford the alcohol **S9** as white solid (11.4 g, 46.0 mmol, 79%). Analytical data in agreement with the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 8.1, 1.6 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 1H), 8.37 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.90 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.70 – 7.57 (m, 4H), 2.93 (dddd, *J* = 12.1, 9.0, 6.0, 2.9 Hz, 2H), 2.67 (m, *J* = 9.3, 6.8, 2.9 Hz, 2H), 2.18 (m, *J* = 11.2, 9.3, 5.7 Hz, 1H), 1.75 (m, *J* = 11.1, 8.8, 6.9 Hz, 1H).



3,4-Dihydrotriphenylen-1(2*H*)-one. A solution of **S9** (11.3 g, 46.0 mmol), in a water-acetonitrile mixture (50 mL: 50 mL) was stirred in an open round-bottom flask at 0 °C for 2 min. Subsequently, $Ce(NH_4)_2(NO_3)_6$ (63.0 g, 94.2 mmol) was added, and the mixture was stirred at 0 °C for 1 h. Then, saturated sodium thiosulfate (100 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate (3x50 mL) and the combined organic layers were washed with water, brine, dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 20:1) to afford a yellow semisolid product **S10** (6.50 g, 26.2 mmol, 57%). Analytical data in according to the literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 – 9.22 (m, 1H), 8.73 – 8.63 (m, 2H), 8.25 – 8.18 (m, 1H), 7.76 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.71 – 7.60 (m, 3H), 3.44 (t, *J* = 6.2 Hz, 2H), 2.85 (dd, *J* = 7.5, 6.0 Hz, 2H), 2.36 – 2.27 (m, 2H).

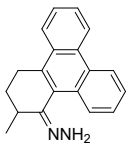


2-Methyl-3,4-dihydrotriphenylen-1(2*H*)-one. To a solution of LDA (22.0 mL, 2 M, 44.0 mmol) in THF (20 mL) under a N_2 atmosphere at -78 °C, hexamethylphosphoramide (HMPA, 10.0 mL) was added dropwise, and the mixture was stirred for 2 h. A solution of **S10** (4.9 g, 20.0 mmol) in THF (20 mL) was added dropwise, and the mixture was stirred at -78 °C for 2 h. After addition of iodomethane (2.4 mL, 37.4 mmol), the mixture was stirred overnight to room temperature. The reaction was quenched with aqueous NH_4Cl, and the mixture was extracted with ethyl acetate (50 mL). The organic layer was washed with aqueous $NaHCO_3$, water, and brine, dried with anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane:CH_2Cl_2 =3:1) to afford slight yellow solid product **S11** (2.20 g, 7.70 mmol, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 – 9.15 (m, 1H), 8.73 – 8.63 (m, 2H), 8.19 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.75 (ddd, *J* = 8.3, 7.0, 1.3 Hz, 1H), 7.70 – 7.60 (m, 3H), 3.57 (ddd, *J* = 17.7, 5.3, 3.8 Hz, 1H), 3.37 (ddd, *J* = 17.7, 10.5, 5.4 Hz, 1H), 2.93 – 2.81 (m, 1H), 2.43 (dtd, *J* = 13.7, 5.2, 3.9 Hz, 1H), 2.12 – 1.97 (m, 1H), 1.35 (d, *J* = 6.7 Hz, 3H).

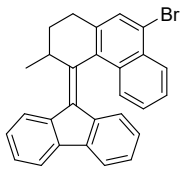
^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 142.9, 132.4, 130.2, 130.1, 129.0, 128.9, 127.9, 127.8, 127.4, 127.2, 126.6, 125.4, 123.2, 122.5, 43.3, 30.6, 26.4, 15.8.

HRMS (ESI pos) calcd $C_{19}H_{17}O$ $[M+H]^+$: 261.1274, found 261.1271.



(*E/Z*)-(2-Methyl-3,4-dihydrotriphenylen-1(2*H*)-ylidene)hydrazine. The **S11** (0.650 g, 2.50 mmol) was dissolved in EtOH and $NH_2NH_2{\cdot}H_2O$ (15 ml + 15 mL) and the mixture was heated under reflux at 90 °C for 6 d. The mixture was extracted with ethyl acetate (20 mL) and washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 3:1) to afford slightly yellow solid **S12** (500 mg, 1.80 mmol, 73%).

HRMS (ESI pos) calcd $C_{19}H_{19}N_2$ $[M+H]^+$: 275.1543, found 275.1544.

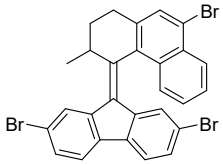


9-Bromo-4-(9H-fluoren-9-ylidene)-3-methyl-1,2,3,4-tetrahydrophenanthrene. Lawesson's reagent (570 mg, 1.4 mmol) and 9*H*-fluoren-9-one (360 mg, 2.00 mmol) were added to a vial under a N_2 atmosphere. Dry toluene (15 mL) was added, and the reaction mixture was heated at 90 °C for 2 h. After cooling the reaction mixture was directly poured onto a column and the residue was purified by quick column chromatography (SiO_2, pentane:CH_2Cl_2 = 3:1). Thioketone fraction was collected and concentrated under reduced pressure to yield a dark purple solid (to prevent hydrolysis, the product was kept wet with CH_2Cl_2 and was used immediately in the next step). In another two-neck flask under a N_2 atmosphere, hydrazone **S8** (121 mg, 0.4 mmol) was dissolved in DMF (4 mL). The solution was cooled to -40 °C and bis(trifluoroacethoxy)iodobenzene (181 mg, 0.42 mmol) in DMF (3 mL) was added to the stirred solution. The mixture was stirred for 3 min while the color turned from yellow to pink, indicative of the *in situ* formation

of the diazo compound. A solution of the 9*H*-fluoren-9-thione (78.4 mg, 0.4 mmol) in dry CH_2Cl_2 (5 mL) was added to the mixture. The mixture was allowed to warm to room temperature and stirred for 4 h. HMPT (Tris(dimethylamino)phosphine) (0.4 mL) was then added and the mixture stirred for another 24 h. The mixture was diluted with ethyl acetate and washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane: ethyl acetate = 50:1) to afford yellow solid (165 mg, 0.380 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 8.13 – 8.06 (m, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 6.6 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.38 (m, 3H), 7.26 (d, *J* = 15.4 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.58 (t, *J* = 7.7 Hz, 1H), 5.96 (d, *J* = 8.0 Hz, 1H), 4.33 (h, *J* = 7.0 Hz, 1H), 2.73 (dt, *J* = 14.3, 3.6 Hz, 1H), 2.57 (td, *J* = 13.4, 5.2 Hz, 1H), 2.50 – 2.41 (m, 1H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.18 (td, *J* = 12.5, 6.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 141.1, 140.5, 139.7, 138.0, 137.8, 134.18, 133.9, 133.4, 130.8, 130.0, 127.8, 127.7, 127.5, 127.2, 127.2, 126.7, 126.6, 125.7, 125.4, 124.8, 123.5, 119.9, 119.1, 34.7, 31.0, 29.5, 21.0.

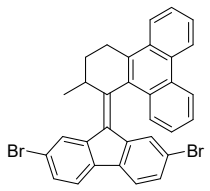


9-Bromo-4-(2,7-dibromo-9*H*-fluoren-9-ylidene)-3-methyl-1,2,3,4-tetrahydrophenanthrene. Lawesson's reagent (814 mg, 2.0 mmol) and 2,7-dibromo-9*H*-fluoren-9-one (340.0 mg, 1.0 mmol) were added to a vial under a N_2 atmosphere. Dry toluene (15 mL) was added, and the reaction mixture was heated at 90 °C for 2 h. After cooling, the reaction mixture was directly poured onto a column and the residue was purified by quick column chromatography (SiO_2, pentane:CH_2Cl_2 = 3:1). The orange thioketone fraction was collected and concentrated under reduced pressure to yield a dark purple solid (126 mg, 0.350 mmol, 35%, to prevent hydrolysis, the product was kept wet with CH_2Cl_2 and was used immediately in the next step). In another two-neck flask under a N_2 atmosphere, hydrazone **S8** (108 mg, 0.360 mmol) was dissolved in DMF (3 mL). The solution was cooled to -40 °C and bis(trifluoroacethoxy)iodobenzene (154 mg, 0.360 mmol) in DMF (3 mL) was added to the stirred solution. The mixture was stirred for 3 min while the color turned from yellow to pink, indicative of the *in situ* formation of the diazo compound. A solution of the 2,7-dibromo-9H-fluoren-9-thione (126.0 mg, 0.35 mmol) in dry CH_2Cl_2 (5 mL) was added to the mixture. The mixture was allowed to warm to room temprature and stirred for 4 h. HMPT (Tris(dimethylamino)phosphine) (0.3 mL) was then added and the mixture stirred for another 24 h. The mixture was diluted with ethyl acetate and washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane:CH_2Cl_2 = 50:1) to afford yellow solid **1** (116 mg, 0.200 mmol, 57%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.33 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 1.7 Hz, 1H), 7.91 – 7.81 (m, 2H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.31 (ddd, *J* = 8.3, 6.8, 1.2 Hz, 1H), 7.20 (dd, *J* = 8.1, 1.7 Hz, 1H), 5.98 (d, *J* = 1.7 Hz, 1H), 4.22 (h, *J* = 7.0 Hz, 1H), 2.79 (ddd, *J* = 14.2, 4.6, 2.9 Hz, 1H), 2.62 – 2.44 (m, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.21 (ddd, *J* = 12.3, 6.5, 4.7 Hz, 1H).

^{13}C NMR (101 MHz, CD_2Cl_2) δ 147.5, 141.4, 139.8, 139.6, 139.0, 137.8, 133.3, 133.1, 132.3, 131.1, 130.9, 130.5, 130.3, 128.7, 128.2, 128.2, 127.9, 127.0, 125.3, 124.3, 121.6, 121.4, 120.9, 120.7, 35.3, 30.9, 29.6, 20.7.

HRMS (APCI pos) calcd $C_{28}H_{19}Br_3$ $[M+H]^+$: 593.9011, found 593.9020.



1-(2,7-Dibromo-9*H*-fluoren-9-ylidene)-2-methyl-1,2,3,4-tetrahydrotriphenylene. Lawesson's reagent (814 mg, 2.00 mmol) and 2,7-dibromo-9*H*-fluoren-9-one (510 mg, 1.50 mmol) were added to a vial under a N_2 atmosphere. Dry toluene (10 mL) was added, and the reaction mixture was heated at 90 °C for 2 h. After cooling, the reaction mixture was directly poured onto a column and the residue was purified by quick column chromatography (SiO_2, pentane:CH_2Cl_2 = 5:1). The orange thioketone fraction was collected and concentrated under reduced pressure to yield a dark purple solid (to prevent hydrolysis, the product was kept wet with CH_2Cl_2 and was used immediately in the next step). In another two-neck flask under a N_2 atmosphere, hydrazone **S12** (90.4 mg, 0.33 mmol) was dissolved in DMF (5 mL). The solution was cooled to -40 °C and bis(trifluoroacethoxy)iodobenzene (146 mg, 0.340 mmol) in DMF (5 mL) was added to the stirred solution. The mixture was stirred for 3 min during which the color of the solution turned from yellow to pink, indicating *in situ* formation of the diazo compound. Then a solution of the 2,7-dibromo-9*H*-fluoren-9-thione (126 mg, 0.350 mmol) in dry CH_2Cl_2 (10 mL) was added to the mixture which was allowed to warm to room temperature and stirred for 4 h. Subsequently, HMPT (Tris(dimethylamino)phosphine) (0.3 mL) was added and the reaction was stirred for another 24 h. Next, the mixture was diluted with ethyl acetate and washed with water, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO_2, pentane:CH_2Cl_2 = 20:1) to afford yellow solid **13** (141 mg, 0.250 mmol, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.78 (d, *J* = 8.4 Hz, 1H), 8.29 – 8.20 (m, 2H), 7.90 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.74 (dddd, *J* = 23.5, 8.2, 6.9, 1.4 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.50 (m, 2H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.32 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.14 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.05 (d, *J* = 1.8 Hz, 1H), 4.31 (h, *J* = 7.0 Hz, 1H), 3.53 (ddd, *J* = 14.6, 4.9, 2.7 Hz, 1H), 2.69 – 2.43 (m, 2H), 1.36 (d, *J* = 6.9 Hz, 3H), 1.33 (dd, *J* = 11.0, 3.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 139.7, 139.3, 138.8, 137.3, 137.3, 131.7, 131.5, 130.9, 130.5, 130.4, 129.8, 129.8, 129.3, 128.7, 128.4, 127.4, 127.3, 127.1, 126.3, 125.2, 124.8, 123.6, 123.2, 121.3, 121.0, 120.8, 120.1, 35.0, 30.6, 24.0, 20.3.

HRMS (APCI pos) calcd $C_{32}H_{22}Br_2$ $[M+H]^+$: 564.0083, found 564.0084.

Isomerization behavior of switches analyzed by ^{1}H-NMR

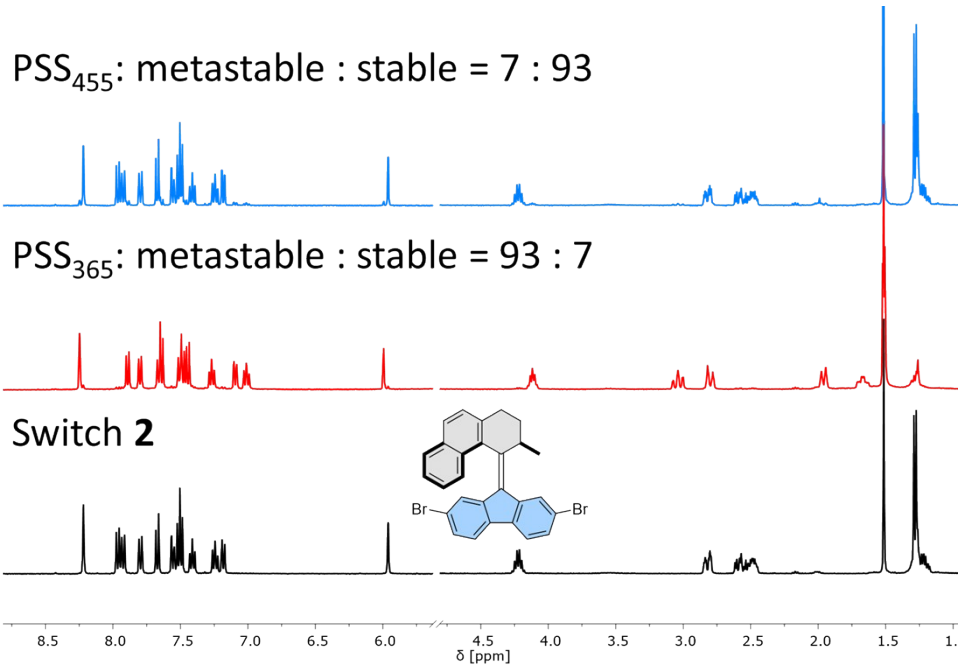


Figure S1. ^{1}H-NMR spectral changes of switch **2** (400 MHz, 298 K, CD_2Cl_2, 5mM) from stable isomer (black, bottom) upon 365 nm irradiation to photostationary state (PSS_{365}, red, middle) then upon 455 nm irradiation to photostationary state (PSS_{455}, blue, top).

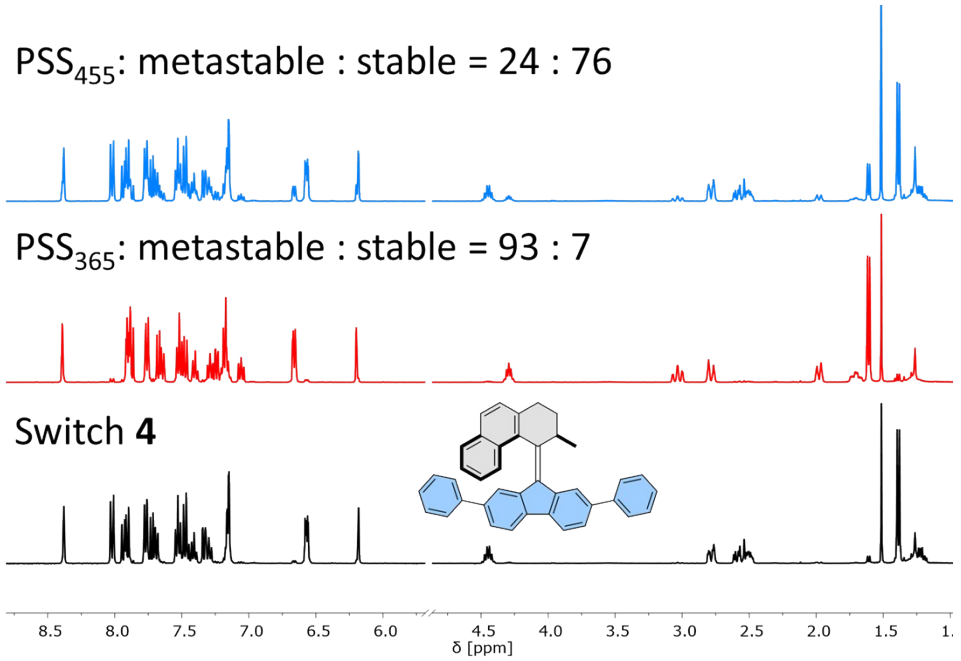


Figure S2. ^{1}H-NMR spectral changes of switch **4** (400 MHz, 298 K, CD_2Cl_2, 5mM) from stable isomer (black, bottom) upon 365 nm irradiation to photostationary state (PSS_{365}, red, middle) then upon 455 nm irradiation to photostationary state (PSS_{455}, blue, top).

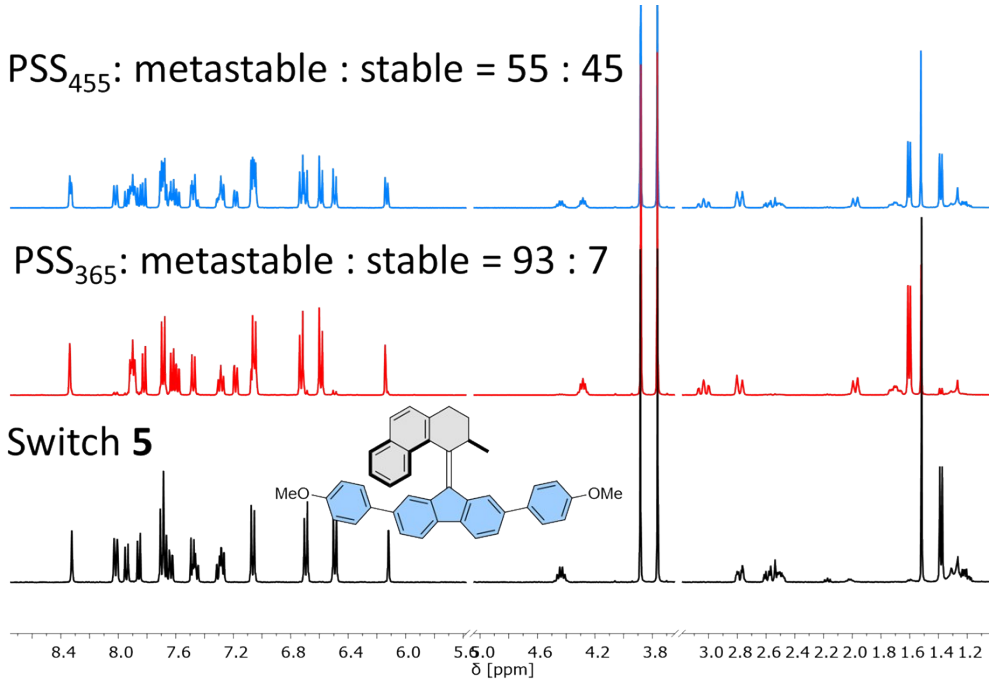


Figure S3. ^{1}H-NMR spectral changes of switch **5** (400 MHz, 298 K, CD_2Cl_2, 5mM) from stable isomer (black) upon 365 nm irradiation to photostationary state (PSS_{365}, red) then upon 455 nm irradiation to photostationary state (PSS_{455}, blue).

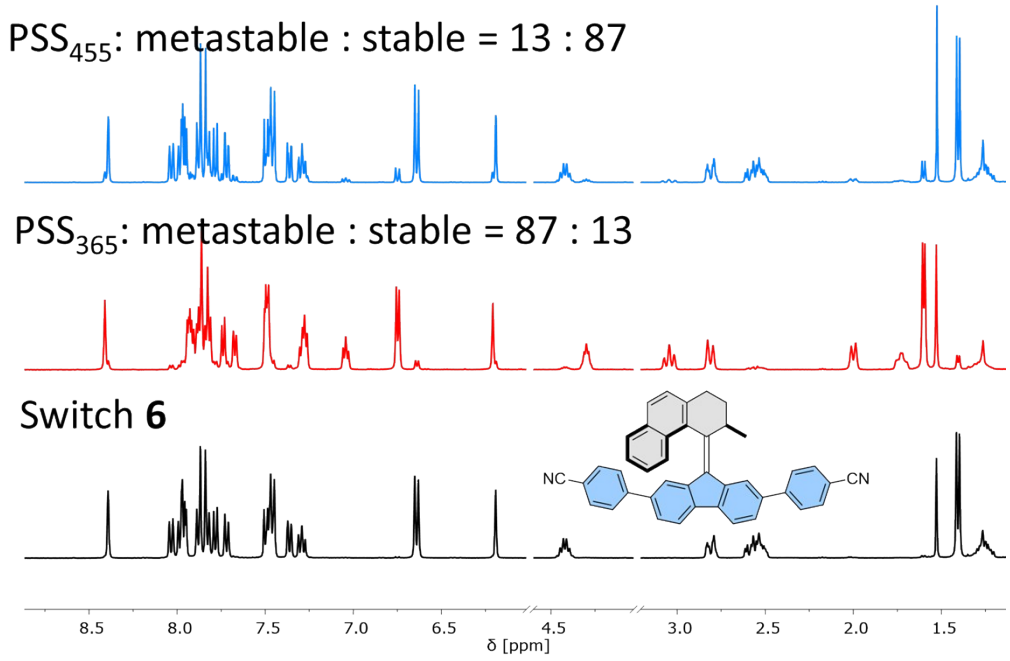


Figure S4. ^{1}H-NMR spectral changes of switch **6** (400 MHz, 298 K, CD_2Cl_2, 5mM) from stable isomer (black, bottom) upon 365 nm irradiation to photostationary state (PSS_{365}, red, middle) then upon 455 nm irradiation to photostationary state (PSS_{455}, blue, top).

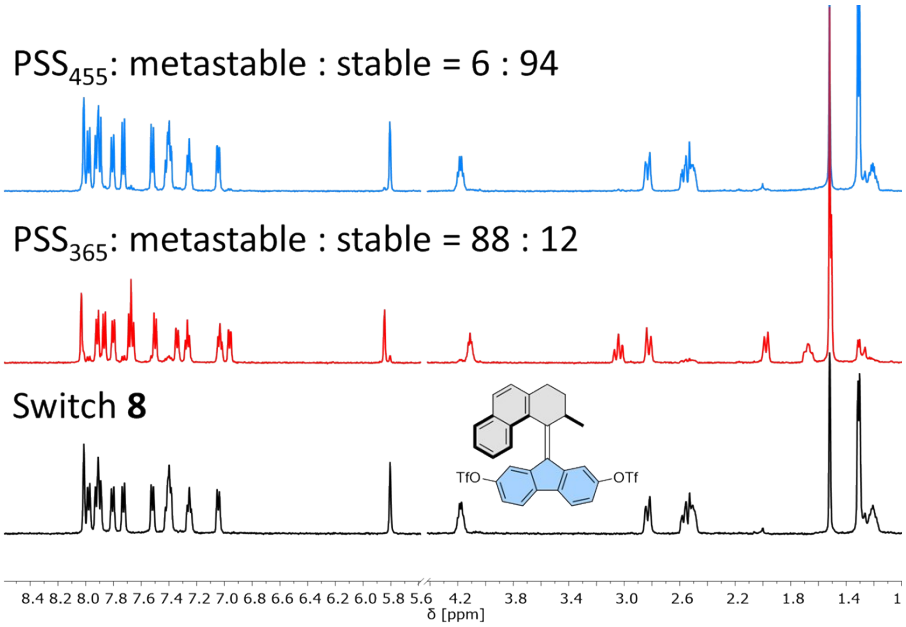


Figure S5. ^{1}H-NMR spectral changes of switch **8** (500 MHz, 298 K, CD_2Cl_2, 5mM) from stable isomer (black, bottom) upon 365 nm irradiation to photostationary state (PSS_{365}, red, middle) then upon 455 nm irradiation to photostationary state (PSS_{455}, blue, top).

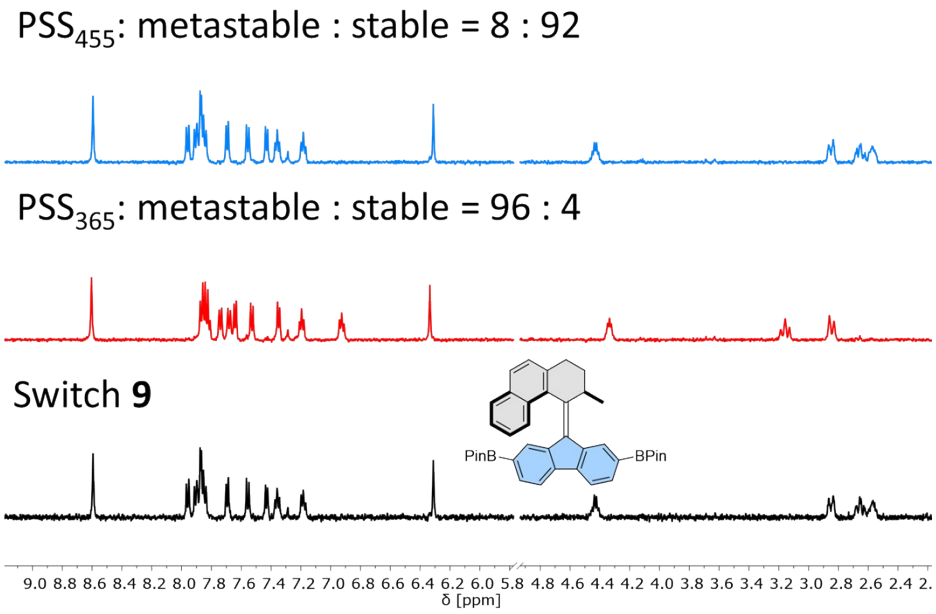


Figure S6. ^{1}H-NMR spectral changes of switch **9** (500 MHz, 298 K, CD_2Cl_2, 2mM) from stable isomer (black, bottom) upon 365 nm irradiation to photostationary state (PSS_{365}, red, middle) then upon 455 nm irradiation to photostationary state (PSS_{455}, blue, top).

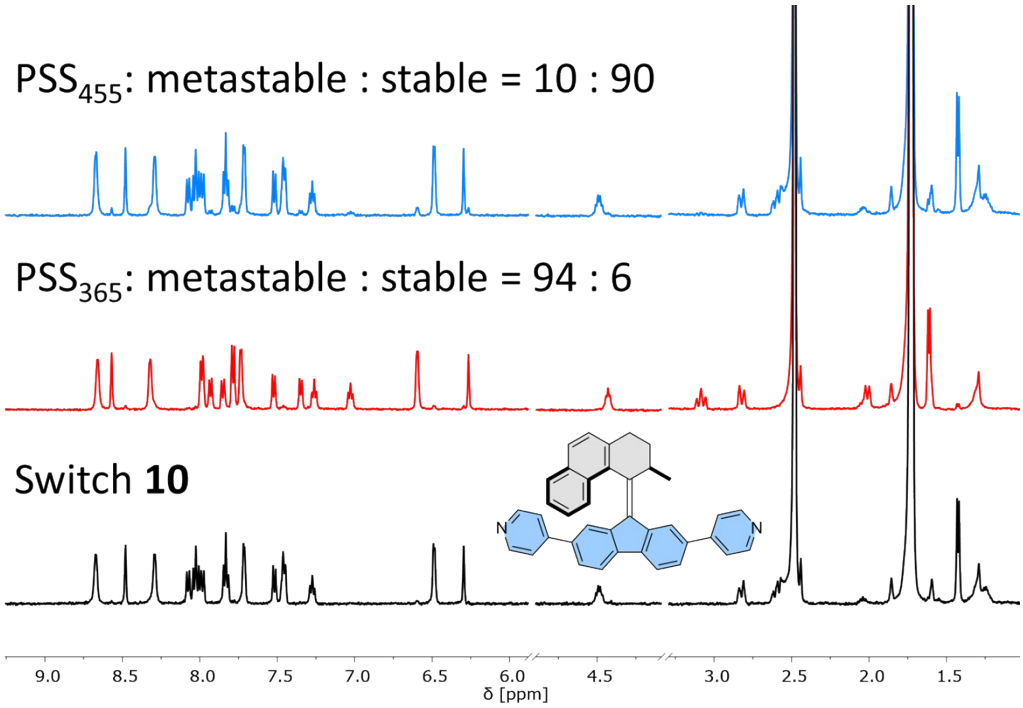


Figure S7. ^{1}H-NMR spectral changes of switch **10** (500 MHz, 298 K, THF-d_8, 5mM) from stable isomer (black, bottom) upon 365 nm irradiation to photostationary state (PSS_{365}, red, middle) then upon 455 nm irradiation to photostationary state (PSS_{455}, blue, top).

Isomerization behavior of chiral switch 1 analyzed by CD and UV spectroscopies.

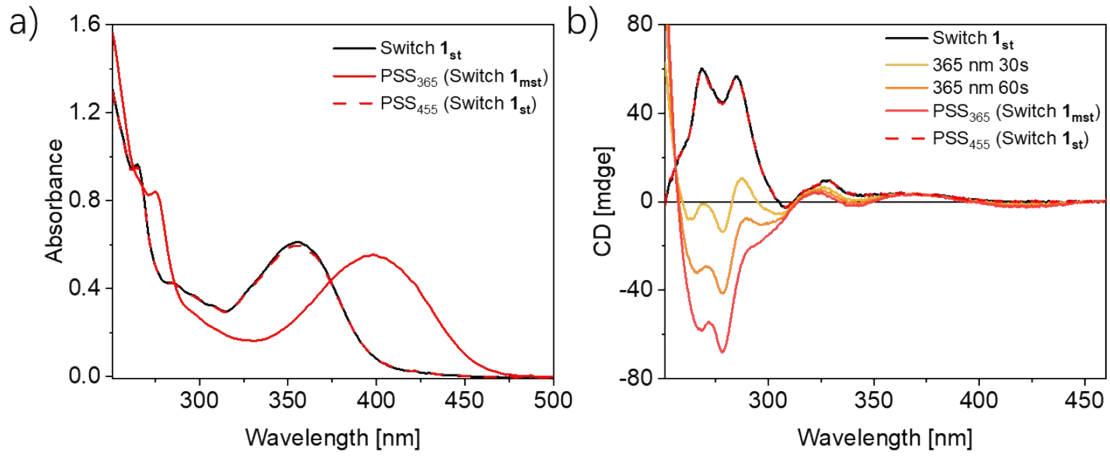


Figure S8. a) UV and b) CD spectral changes of chiral switch **1** (298 K,CH_2Cl_2, 42 μM) from stable isomer (black solid line) upon 365 nm irradiation to photostationary state (PSS_{365}, red solid line) then upon 455 nm irradiation to photostationary state (PSS_{455}, red dash line). The absolute stereochemistry (*P*,*R*) of the enantiomer was assigned based on the comparison to the literature data.[4]

Thermal E/Z back-isomerization behavior of switch 1 followed by UV spectroscopy.

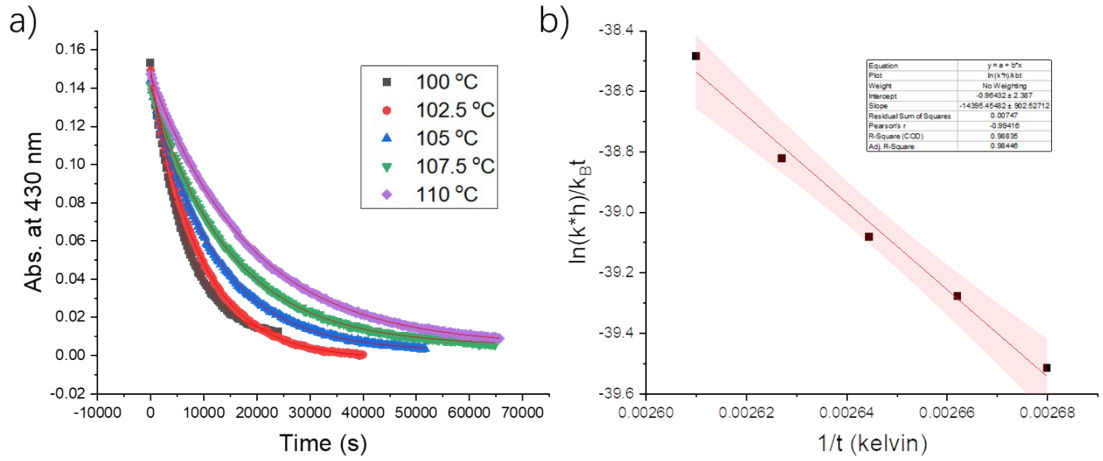


Figure S9. a) Kinetic studies of switch **1** (DMSO, 17 µM) from $\mathbf{1}_{mst}$ to $\mathbf{1}_{st}$ followed by UV spectral changes at different temperatures. b) Eyring plot of TEZ isomerization step from $\mathbf{1}_{mst}$ to $\mathbf{1}_{st}$ in DMSO. Dashed lines indicate 95% confidence intervals.

Quantum yield determination.

Ferrioxalate Chemical Actinometry

A modification of a standard protocol was applied for the determination of the photon flux.[6,7] An aqueous H_2SO_4 solution (0.05 M) containing freshly recrystallized $K_3[Fe(C_2O_4)_3]$ (41 mM, 2.0 mL, 1 cm quartz cuvette) was irradiated at 20 °C for a given period of time with exclusion of ambient light with a 365 or a 445 nm LED, under stirring. The solution was then diluted with 1.0 mL of an aqueous H_2SO_4 solution (0.5 M) containing phenanthroline (1 g/L) and NaOAc (122.5 g/L) and left to react for 10 min. The absorption at λ= 510 nm was measured and compared to an identically prepared non-irradiated sample. The experiment was repeated with fresh samples with increasing irradiation times. The concentration of $[Fe(phenanthroline)_3]^{2+}$ complex was calculated using its molar absorptivity (ε = 11100 M^{-1} cm^{-1}) and considering the dilution. The quantity of Fe^{2+} ions expressed in mol was plotted versus time (expressed in seconds, s) and the slope, obtained by linear fitting the data points to the equation y = ax + b, equals the rate of formation of the Fe^{2+} ion at the given wavelength. This rate can be converted into the photon flux (I) by dividing it by the quantum yield of the $[Fe(C_2O_4)_3]^{2+}$ complex at the wavelength of interest (Φ^{365nm} = 1.21, Φ^{445}= 1.18)[8] and by the probability of photon absorption of the Fe^{3+} complex (approximated to **1** for 365 nm LED as we were working in total absorption regime, and 0.85 for the 445 nm LED). The obtained molar photon fluxes were I^{365nm} = $3.95 \cdot 10^{-5}$ mmol s^{-1}, I^{445nm} $2.60 \cdot 10^{-5}$ mmol s^{-1}.

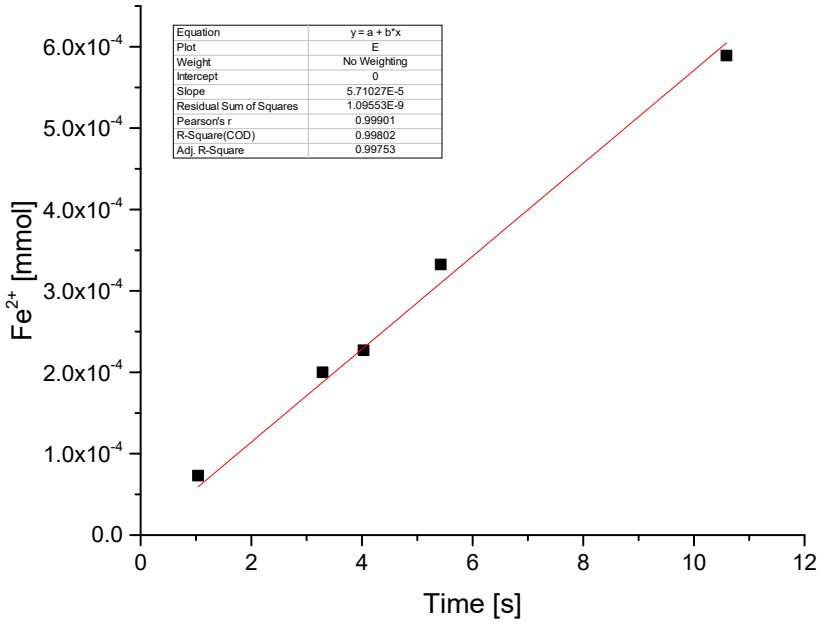


Figure S10. Linear fitting of the Fe^{2+} generated upon irradiation of the $[Fe(phenanthroline)_3]^{2+}$ complex 365 nm at different irradiation times.

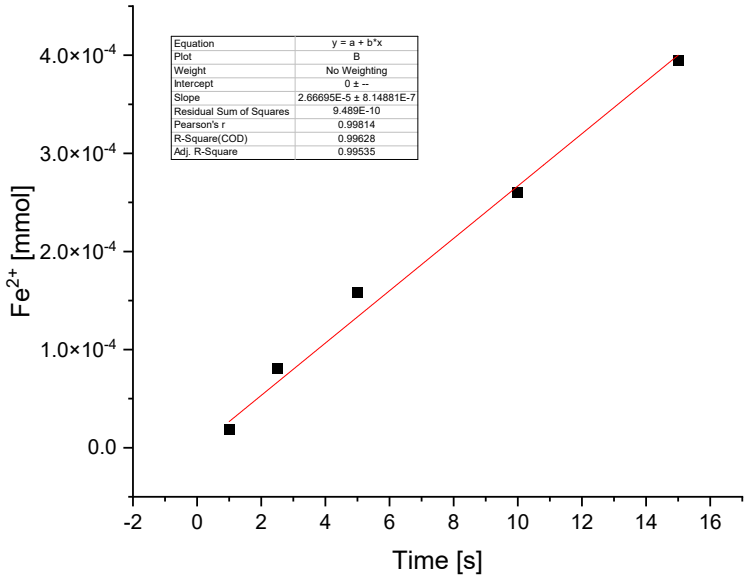


Figure S11. Linear fitting of the Fe^{2+} generated upon irradiation of the $[Fe(phenanthroline)_3]^{2+}$ complex 445 nm at different irradiation times.

Quantum yields determination by UV/Vis method

Photon fluxes for the light sources at 365 nm and 445 nm were determined using standard ferrioxolate actinometry which provided values $3.95 \cdot 10^{-5}$ mmol s^{-1} and $2.60 \cdot 10^{-5}$ mmol s^{-1}, respectively. Evolution of the UV/Vis electronic absorption spectra upon irradiation at specific wavelength with pre-determined photon flux was followed over time. Spectra were processed in SpectraGryph software. Molar attenuation coefficients of the stable isomers of the overcrowded alkenes were determined by recording absorbance for the series of solutions (solvent) at known concentration and least-square fitting these data to the Beer-Lamber law (Table 1). Molar attenuation coefficients of the corresponding metastable diastereomers were calculated from Beer-Lamber law using photostationary state distributions which were established (Figure 3a-3c and Figure S1-S7) by ^{1}H NMR spectroscopy. Quantum yields were determined following the approach developed by Stranius and Börjesson.[9] Time-dependent evolution of the absorbance at the irradiation wavelength was fitted using COPASI 4.30 software to the kinetic equation:

$$\frac{d[MS]}{dt} = -\frac{QY_{365st\rightarrow mst} \cdot I \cdot \beta_{st}(t)}{N_A \cdot V} + \frac{QY_{365mst\rightarrow st} \cdot I \cdot \beta_{mst}(t)}{N_A \cdot V}$$

Where, [MS] is transient concentration of the metastable isomer, $QY_{365st\rightarrow mst}$ is the quantum yield of the isomerization of the stable isomers, $QY_{365mst\rightarrow st}$ is the quantum yield of the isomerization of the metastable isomers upon irradiation at the indicated (365 nm) wavelength, I is the photon flux, previously determined with ferrioxalate actinometry, N_A the Avogadro number, V the total volume of the irradiated solution (2 mL) and β the fractions of photons absorbed by either the stable or the metastable diastereomer. All measurements were performed at least in duplicates.For the metastable isomer:

$$\frac{d[S]}{dt} = -\frac{QY_{445mst\rightarrow st} \cdot I \cdot \beta_{mst}(t)}{N_A \cdot V} + \frac{QY_{445st\rightarrow mst} \cdot I \cdot \beta_{st}(t)}{N_A \cdot V}$$

Where, [S] is transient concentration of the stable isomer, $QY_{445mst\rightarrow st}$ is the quantum yield of the isomerization of the metastable diastereomer, $QY_{455st\rightarrow sst}$ is the quantum yield of the isomerization of the metastable diastereomer upon irradiation at the indicated (445 nm) wavelength.

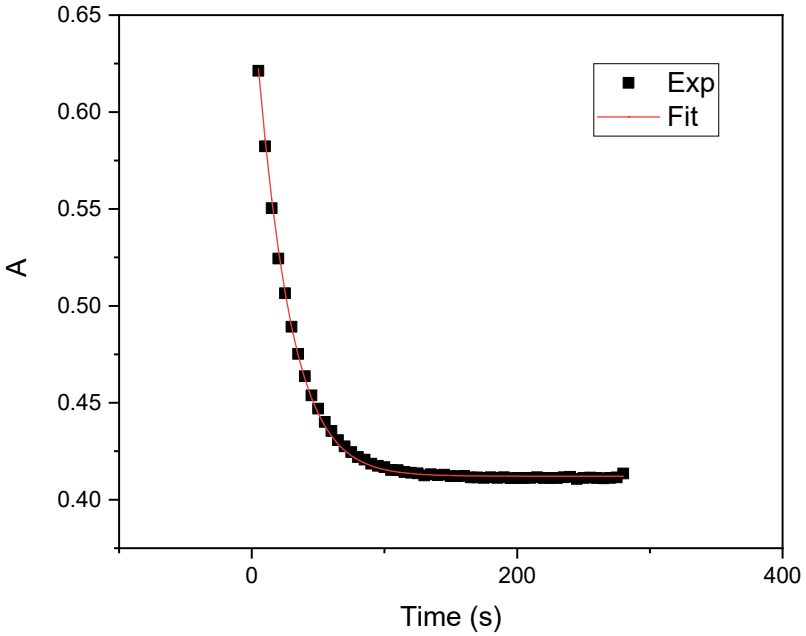


Figure S12. Evolution of the absorbance at 365 nm during the irradiation of **1** in DCM at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

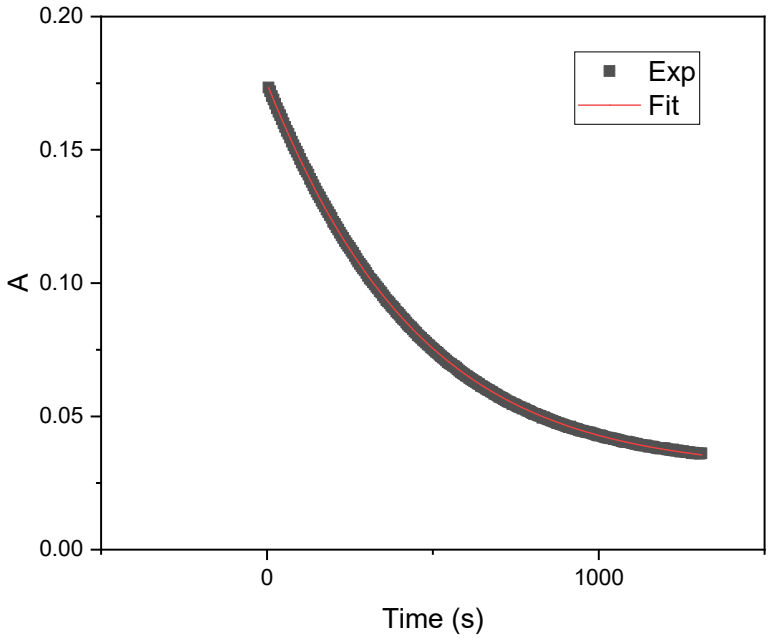


Figure S13. Evolution of the absorbance at 445 nm during the irradiation of **1** in DCM at 445 nm (squares). The red line represents the fit obtained with the ODE solver from COPASI

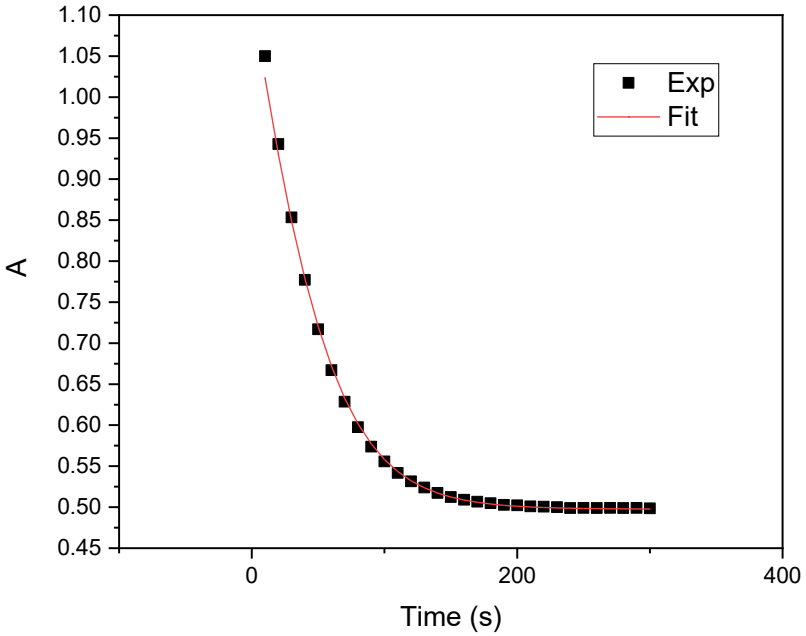


Figure S14. Evolution of the absorbance at 365 nm during the irradiation of **2** in DCM at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

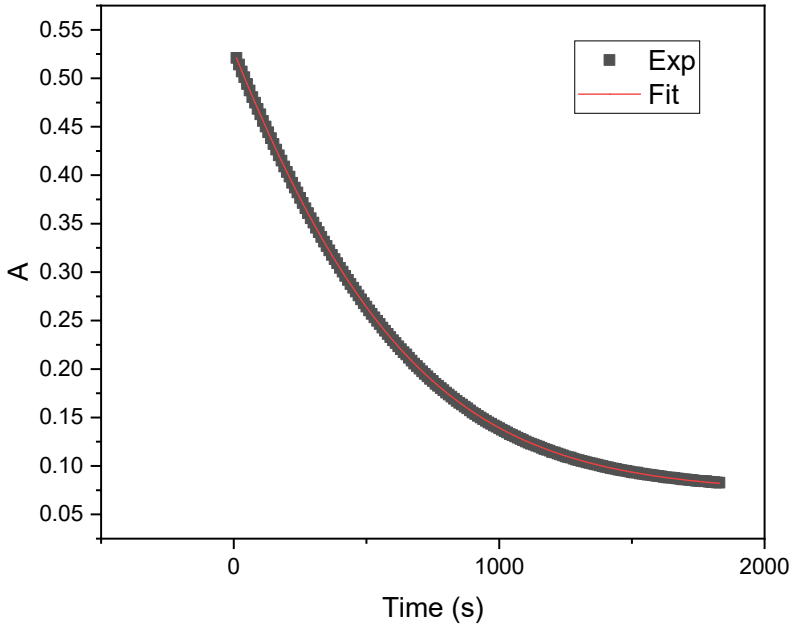


Figure S15. Evolution of the absorbance at 445 nm during the irradiation of **2** in DCM at 445 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

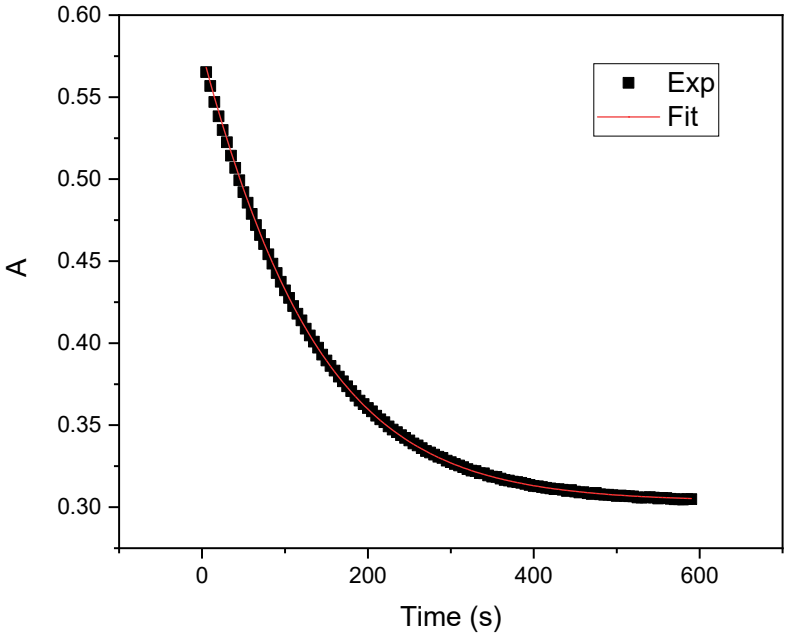


Figure S16. Evolution of the absorbance at 365 nm during the irradiation of **3** in DCM at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

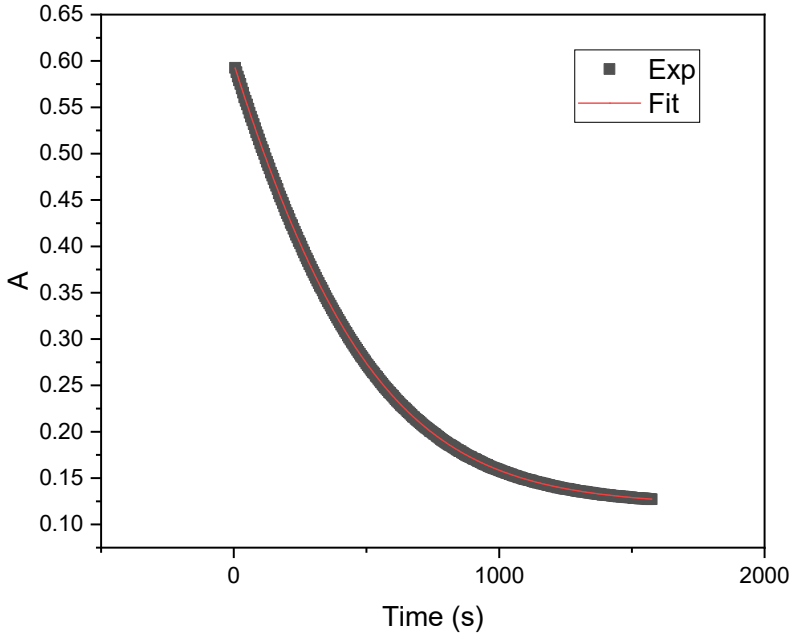


Figure S17. Evolution of the absorbance at 445 nm during the irradiation of **3** in DCM at 445 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

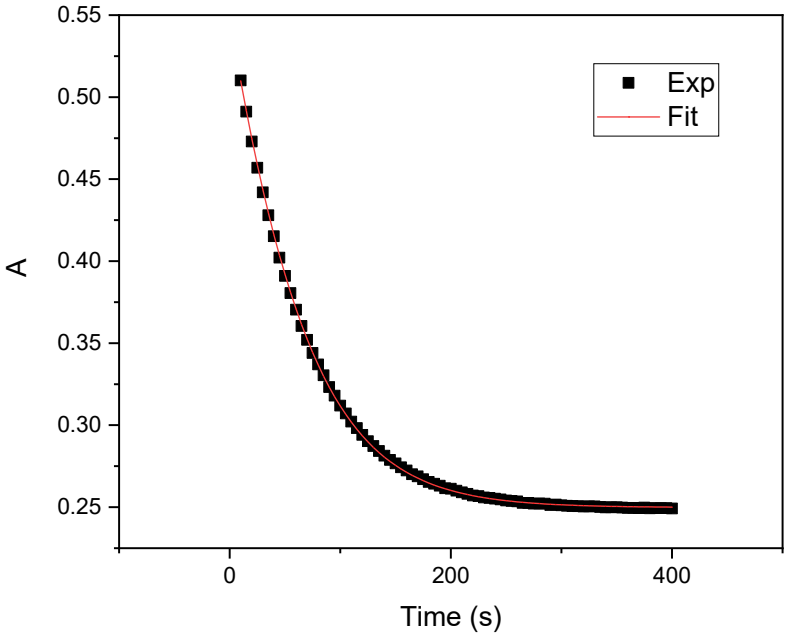


Figure S18. Evolution of the absorbance at 365 nm during the irradiation of **4** in DCM at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

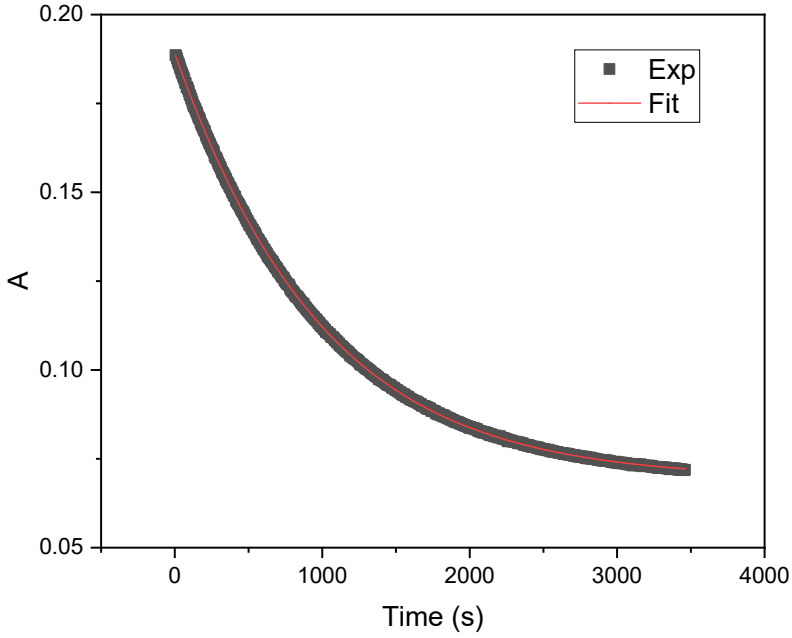


Figure S19. Evolution of the absorbance at 445 nm during the irradiation of **4** in DCM at 445 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

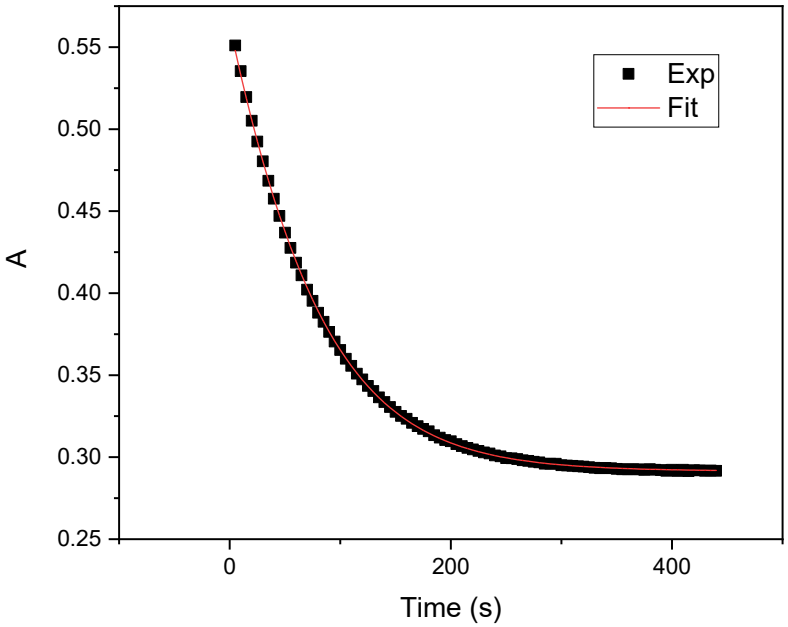


Figure S20. Evolution of the absorbance at 365 nm during the irradiation of **5** in DCM at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

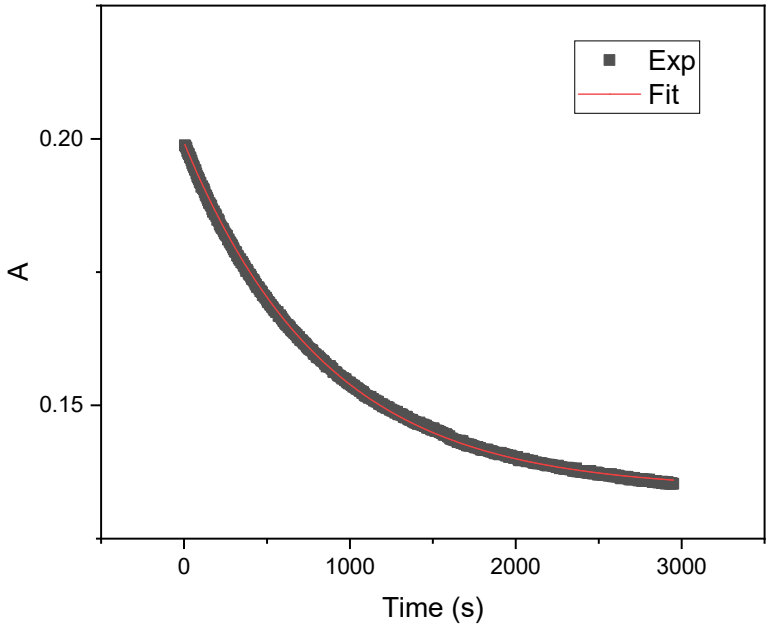


Figure S21. Evolution of the absorbance at 445 nm during the irradiation of **5** in DCM at 445 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

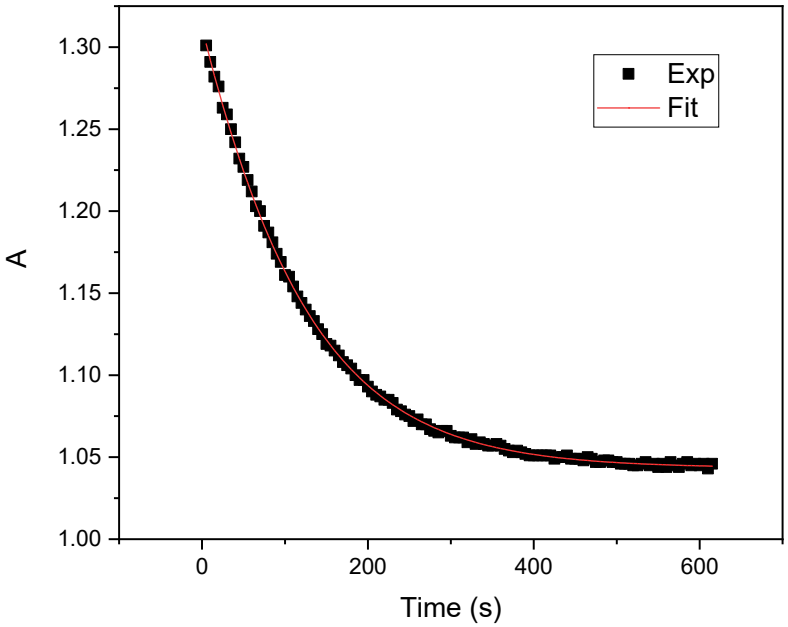


Figure S22. Evolution of the absorbance at 365 nm during the irradiation of **6** in DCM at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

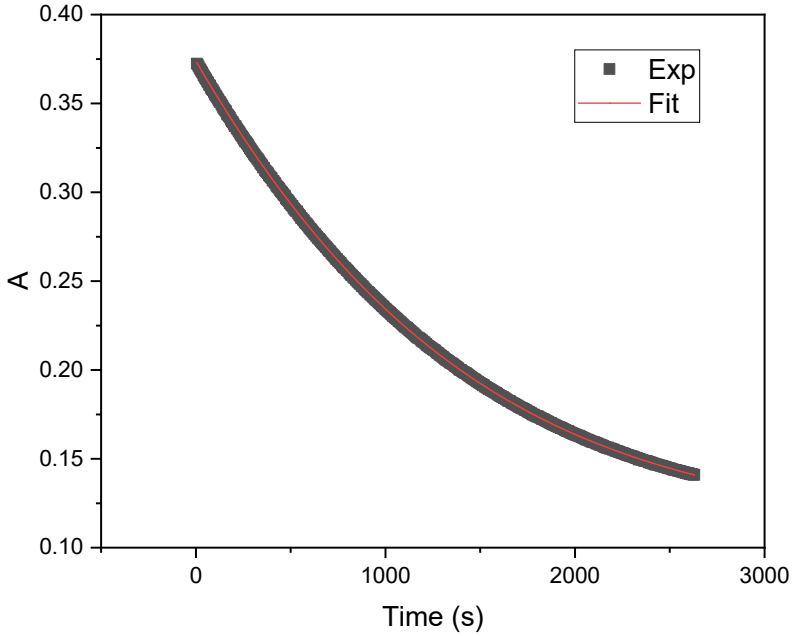


Figure S23. Evolution of the absorbance at 445 nm during the irradiation of **6** in DCM at 445 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

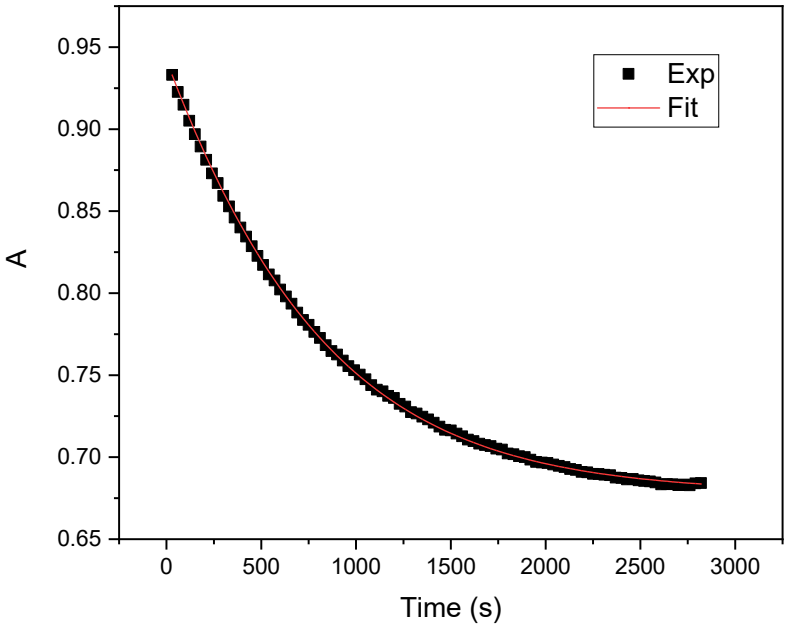


Figure S24. Evolution of the absorbance at 365 nm during the irradiation of **7** in DCM at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

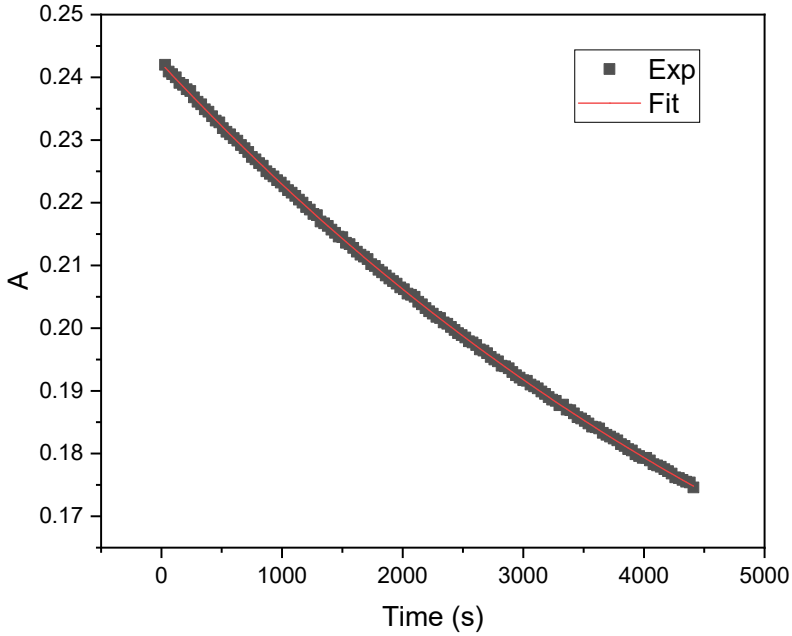


Figure S25. Evolution of the absorbance at 445 nm during the irradiation of **7** in DCM at 445 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

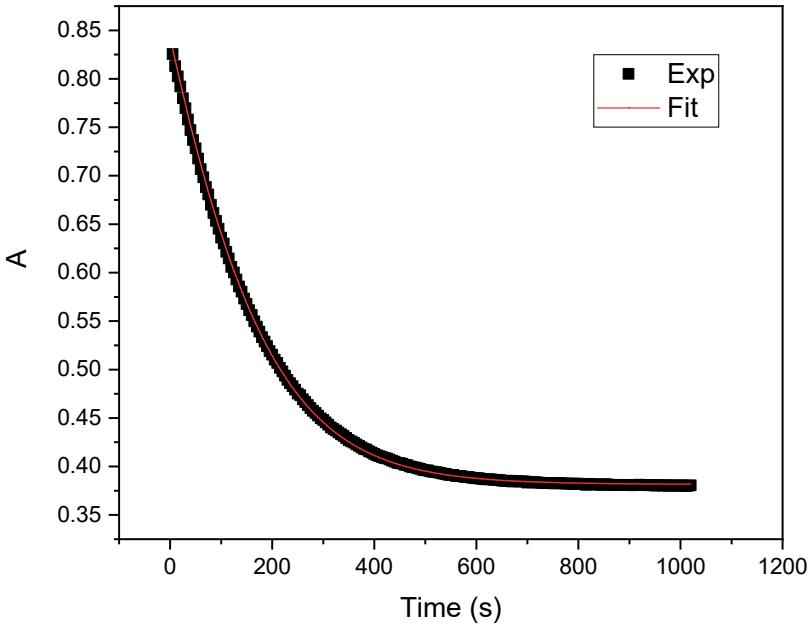


Figure S26. Evolution of the absorbance at 365 nm during the irradiation of **8** in DCM at 365 nm (black lsquares). The red line represents the fit obtained with the ODE solver from COPASI

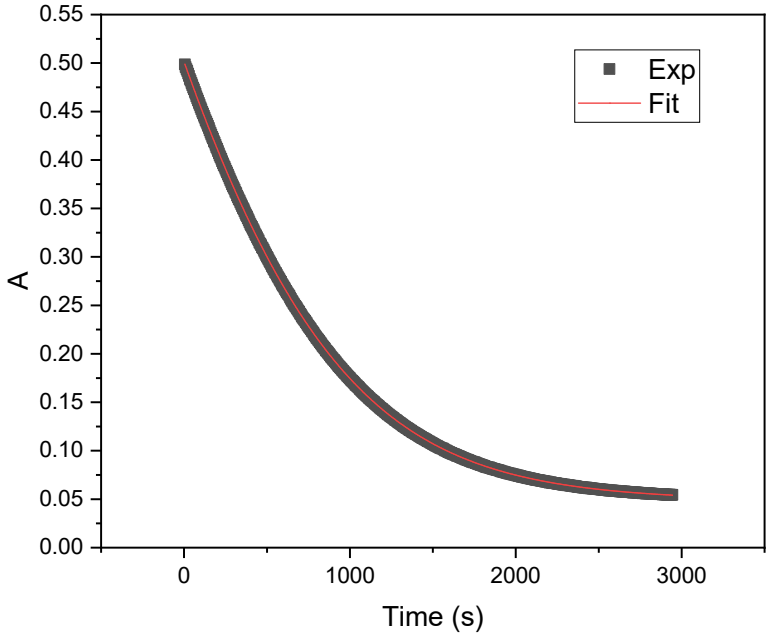


Figure S27. Evolution of the absorbance at 445 nm during the irradiation of **8** in DCM at 445 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

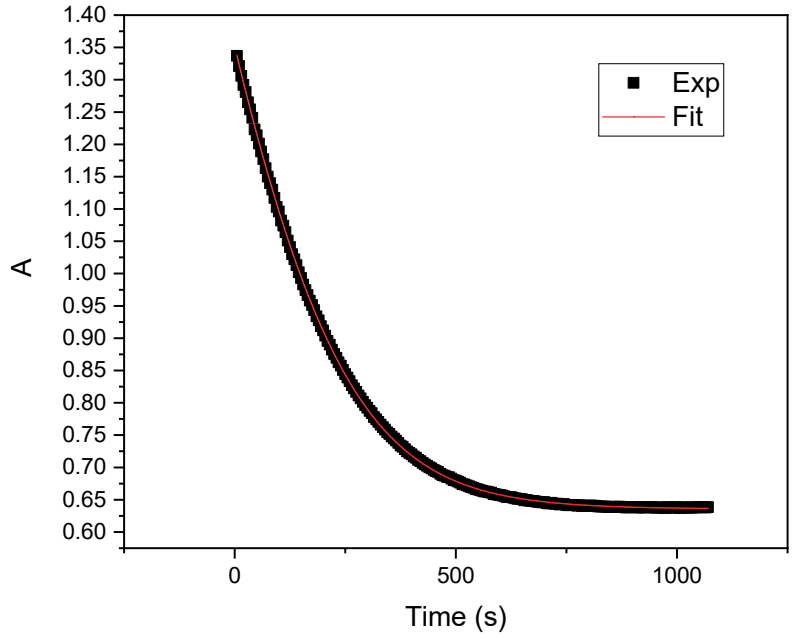


Figure S28. Evolution of the absorbance at 365 nm during the irradiation of **9** in DCM at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

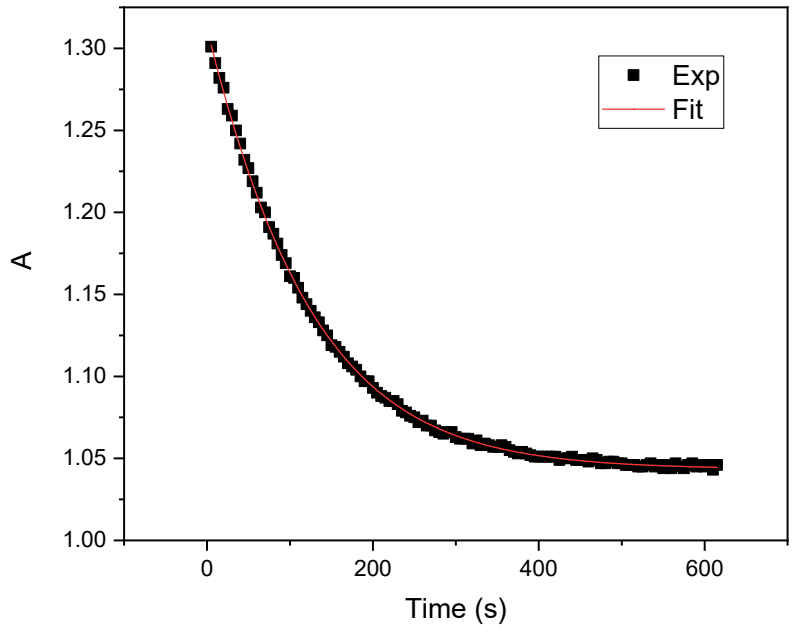


Figure S29. Evolution of the absorbance at 365 nm during the irradiation of **10** in THF at 365 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

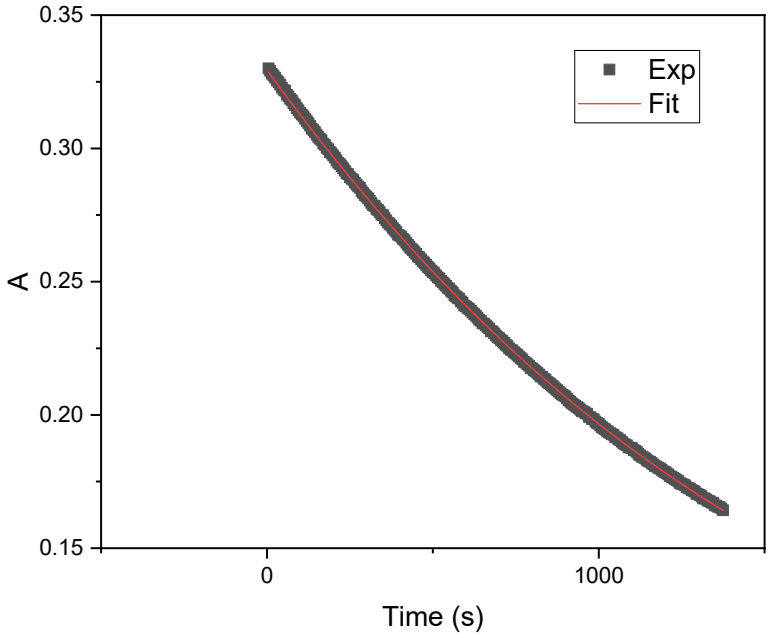


Figure S30. Evolution of the absorbance at 445 nm during the irradiation of **10** in THF at 445 nm (black squares). The red line represents the fit obtained with the ODE solver from COPASI

Computational details

Computational analysis was employed to optimize the thermal pathways of the H-, CN- and MeO- substituted switches**1**,**3** and **7**. The geometries were optimized at the r^{2}SCAN-3c level of theory[10] as implemented in the ORCA 5.0.3 software.[11] The nature of the stationary point was confirmed by means of frequency calculations. The electronic energy of all stationary points was refined at the ωB97X-D3BJ/def2-QZVP level.[12–16] Two main pathways were considered: a thermal E/Z isomerization ($\mathbf{T_{EZ}}$) from the metastable isomer ($\mathbf{M_{eq}}$) back to the initial stable state (**S** in Figure 3d) from which the metastable was formed photochemically, and the thermal helix inversion (**THI**) from the metastable state to the subsequent stable state (**S'**), as the ratcheting step of a motor action. The *E*/*Z* isomerization transition state was modelled using broken-symmetry DFT. Two metastable states were found, each of them differing in the conformation of the chiral methyl (one in axial, $\mathbf{M_{ax}}$, and one in equatorial position $\mathbf{M_{eq}}$, the latter more energetic). The two conformers are separated by a low energetic barrier ($\mathbf{TS_{M\text{-}M}}$). Each conformer is connected to the stable state **S'** with a THI transition state ($\mathbf{THI_{ax}}$ and $\mathbf{THI_{eq}}$, respectively), which in all cases results to be higher in energy than the *E*/*Z* transition state to populate the initial stable state **S**, confirming the nature of these molecules as photoswitches. The substitution does not affect the relative energies between the minima or the THI. On the other hand, a substituent effect can be predicted on the $\mathbf{T_{EZ}}$, where the electron-withdrawing CN raises the barrier by ca. 2 kcal/mol.

HRMS spectra of all compounds

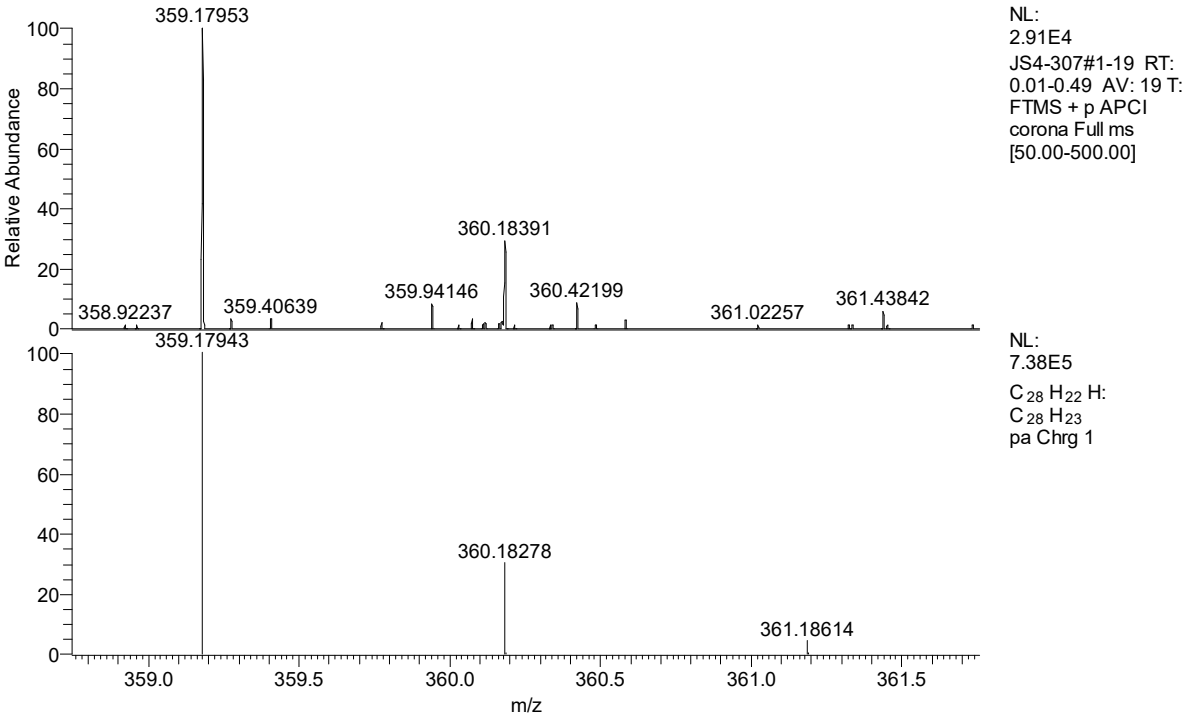


Figure S31. HRMS (ESI pos) spectra of **1** (top:measured, bottom: calcd.).

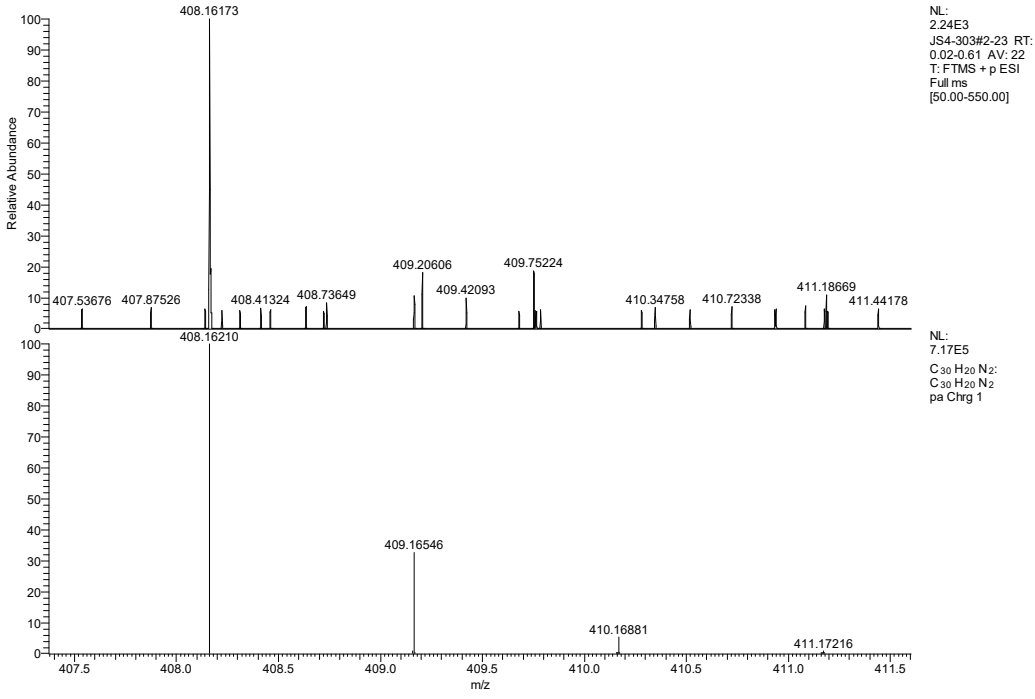


Figure S32. HRMS (ESI pos) spectra of **3** (top:measured, bottom: calcd.).

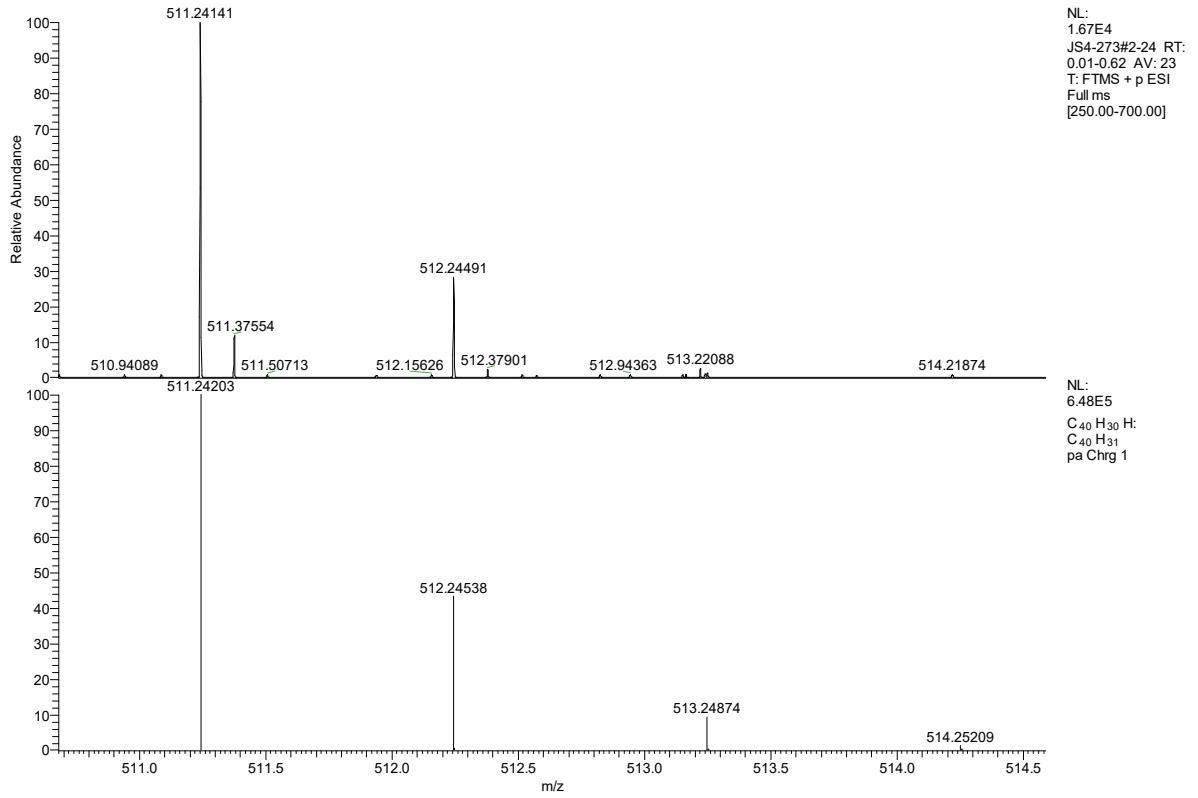


Figure S33. HRMS (ESI pos) spectra of **4** (top:measured, bottom: calcd.).

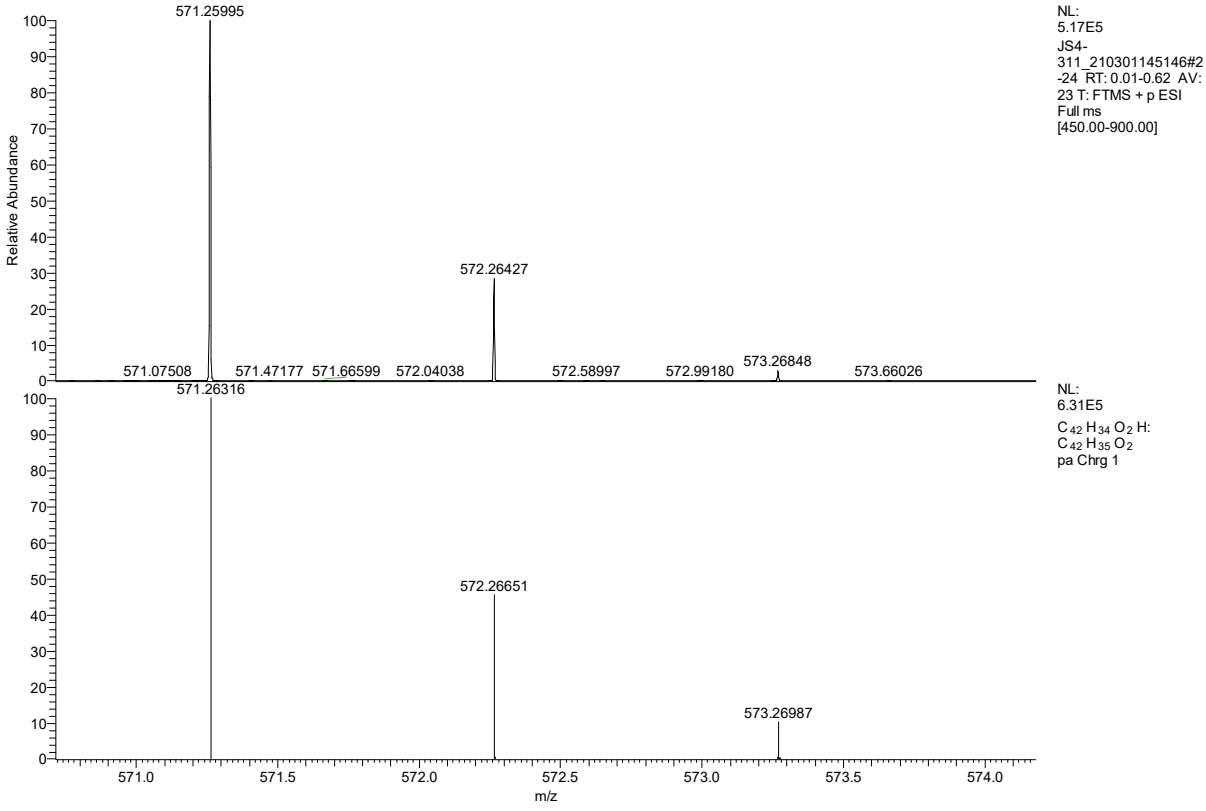


Figure S34. HRMS (ESI pos) spectra of **5** (top:measured, bottom: calcd.).

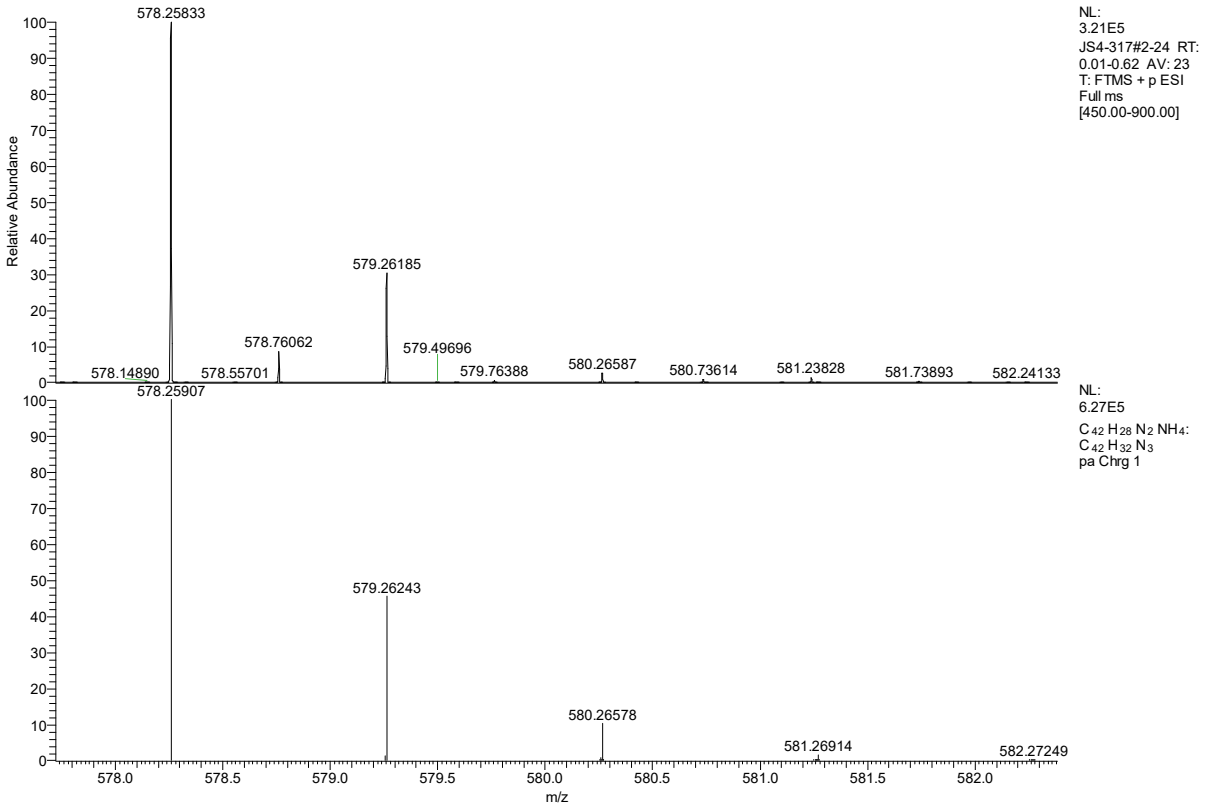


Figure S35. HRMS (ESI) spectra of **6** (top:measured, bottom: calcd.).

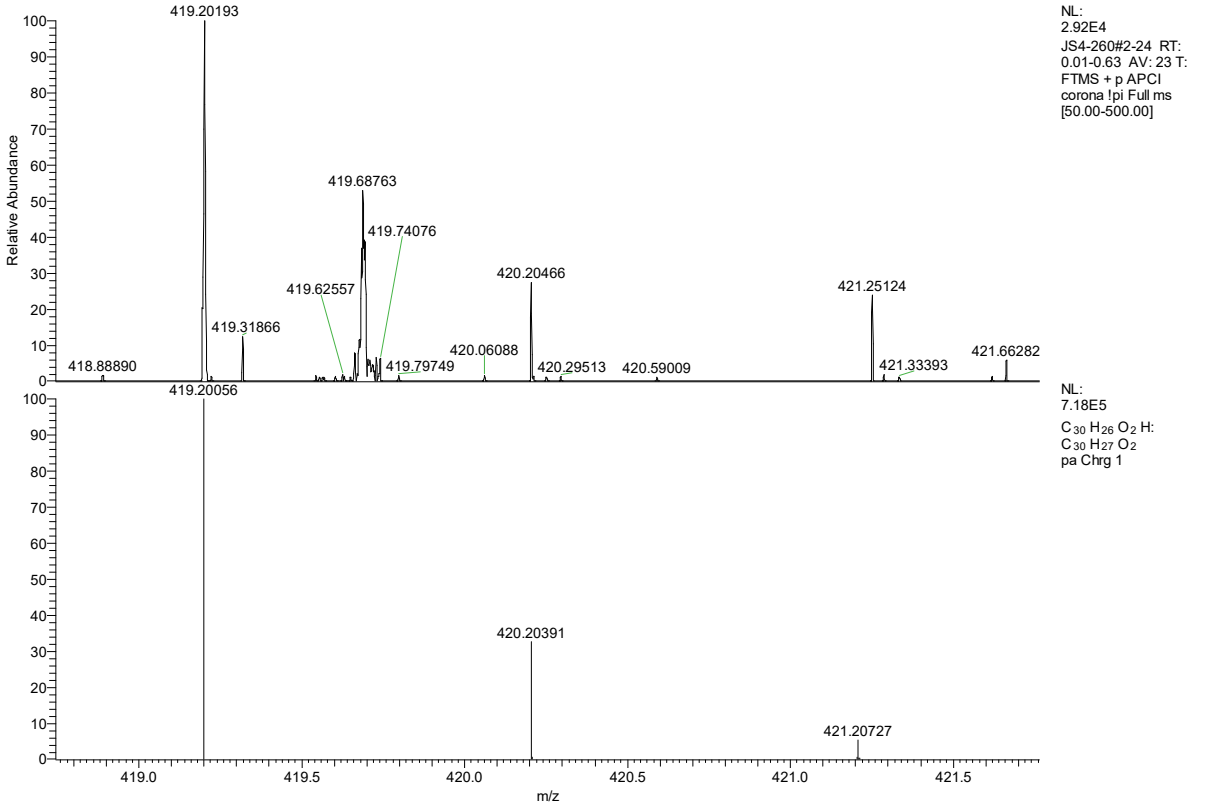


Figure S36. HRMS (APCI pos) spectra of **7** (top:measured, bottom: calcd.).

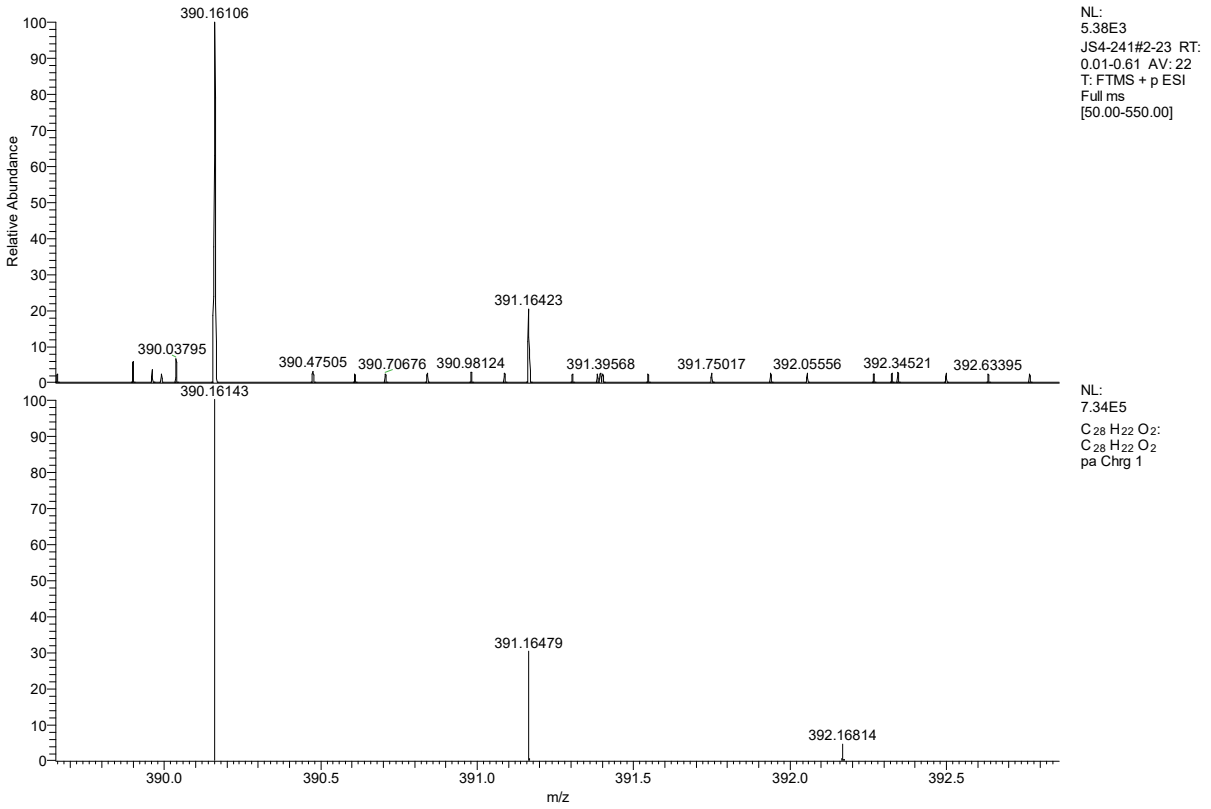


Figure S37. HRMS (ESI) spectra of **7'**(top:measured, bottom: calcd.).

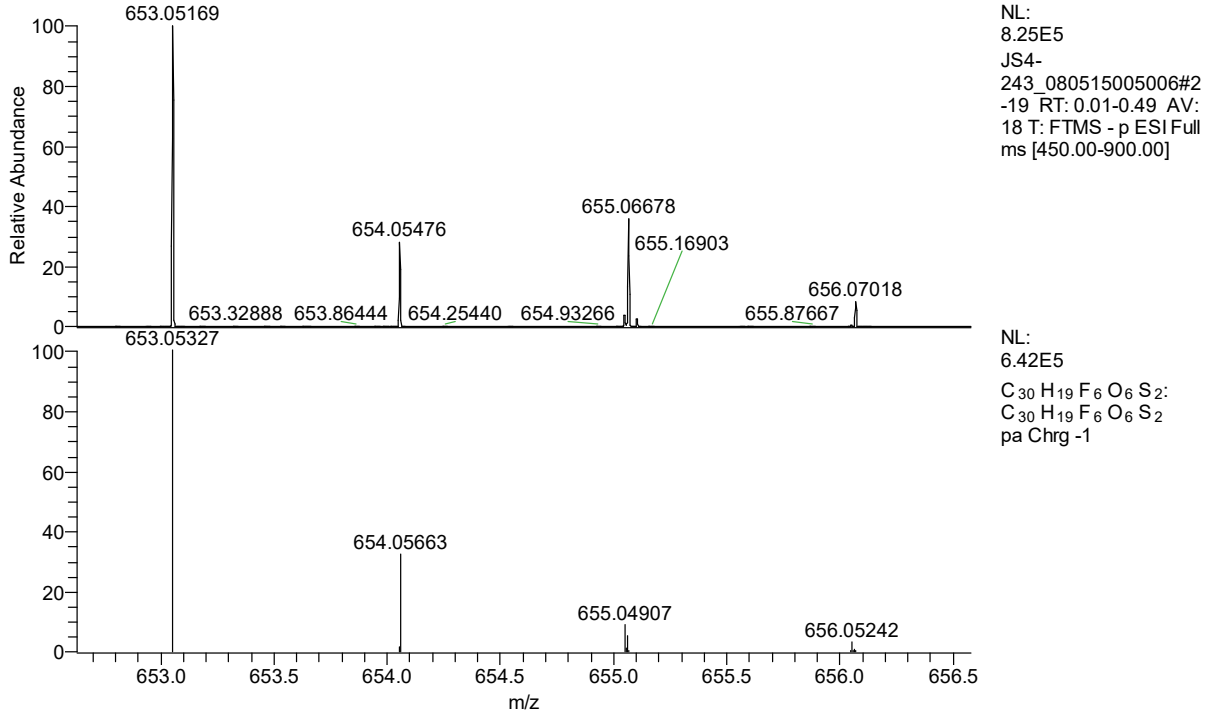


Figure S38. HRMS (ESI neg) spectra of **8** (top:measured, bottom: calcd.).

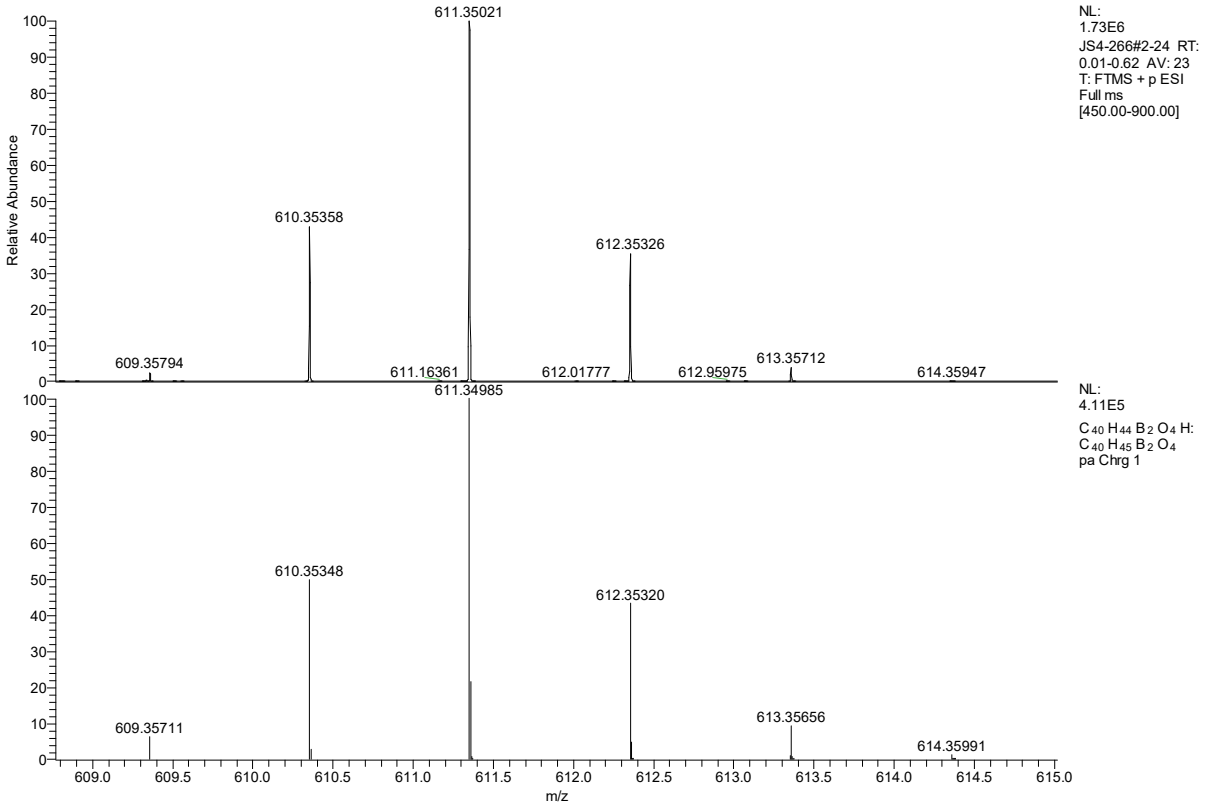


Figure S39. HRMS (ESI pos) spectra of **9** (top:measured, bottom: calcd.).

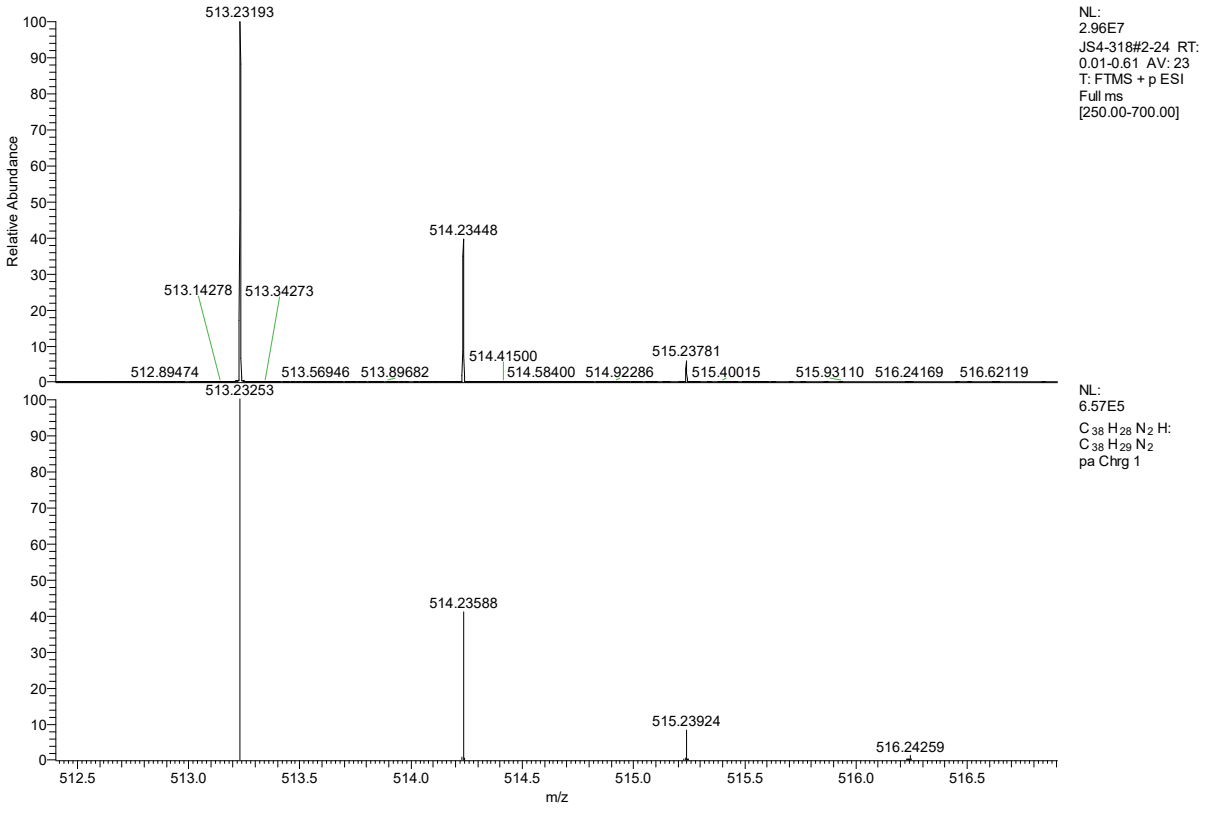


Figure S40. HRMS (ESI pos) spectra of **10** (top:measured, bottom: calcd.).

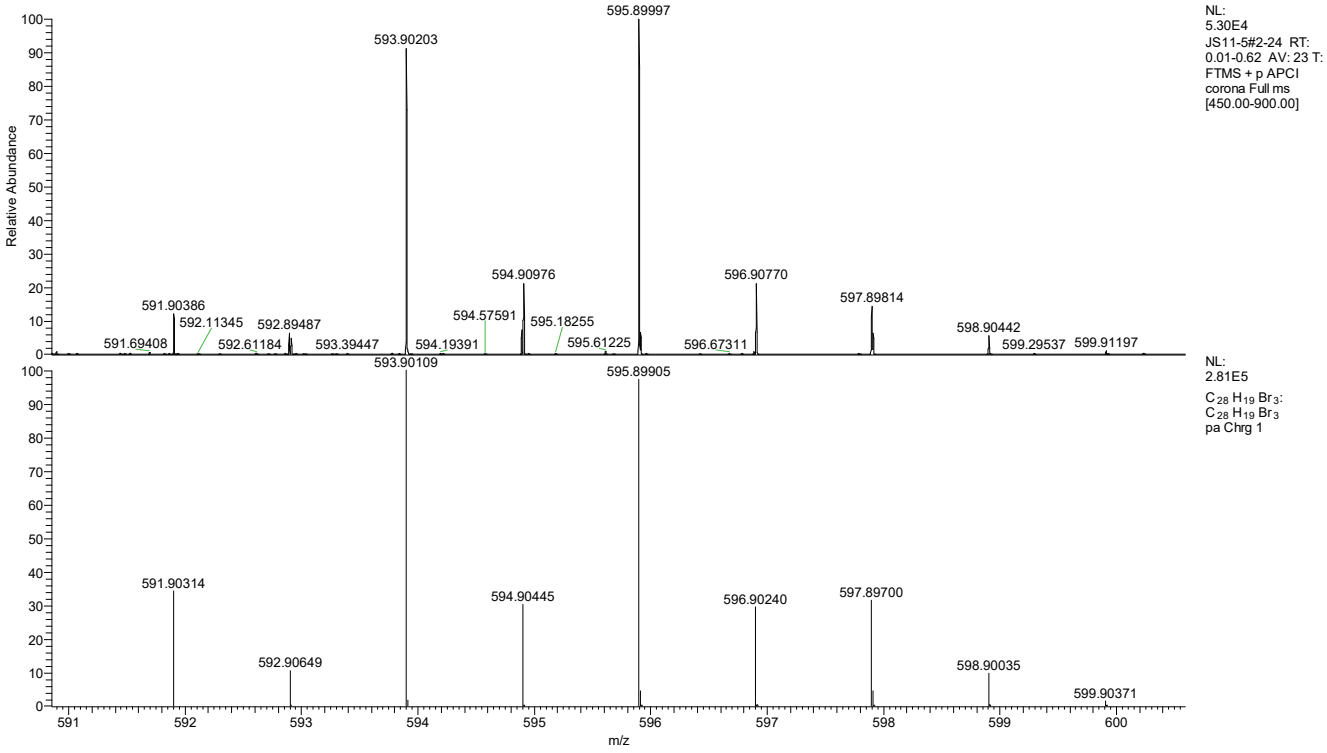


Figure S41. HRMS (ESI pos) spectra of **12** (top:measured, bottom: calcd.).

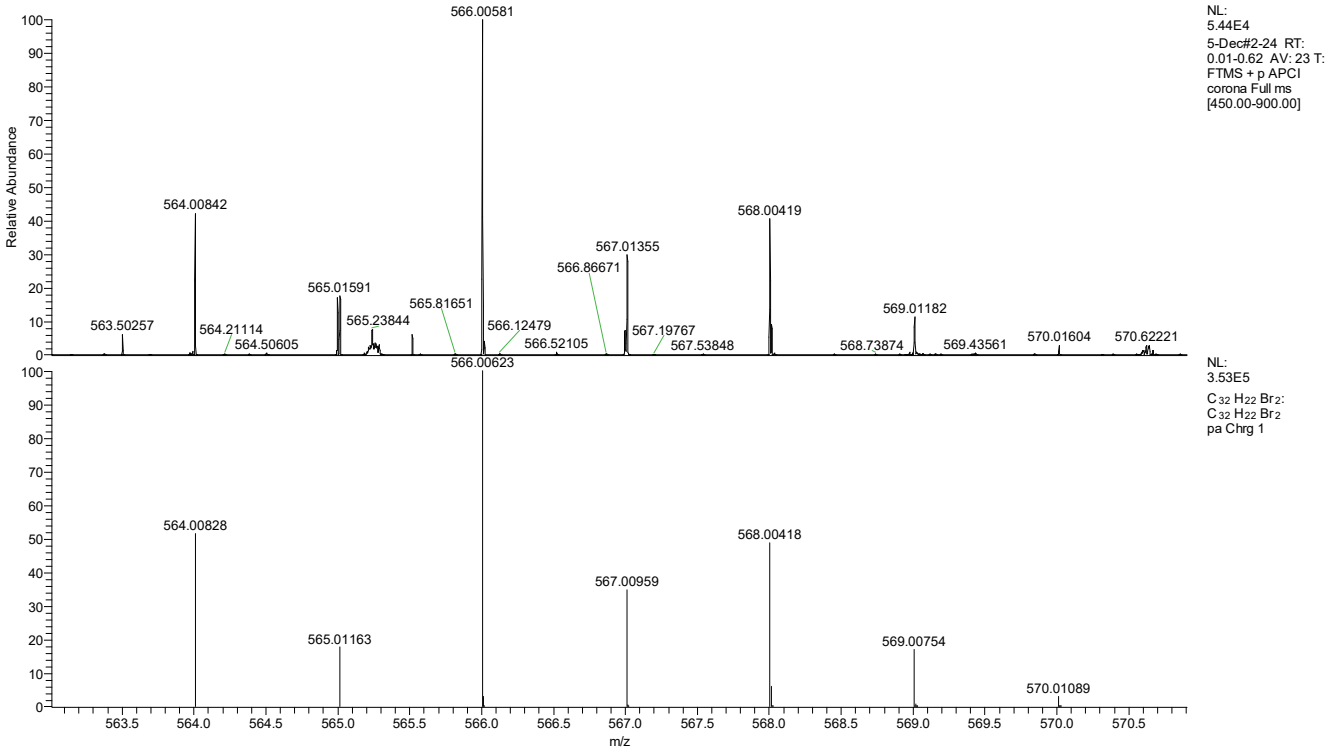


Figure S42. HRMS (ESI pos) spectra of **13** (top:measured, bottom: calcd.).

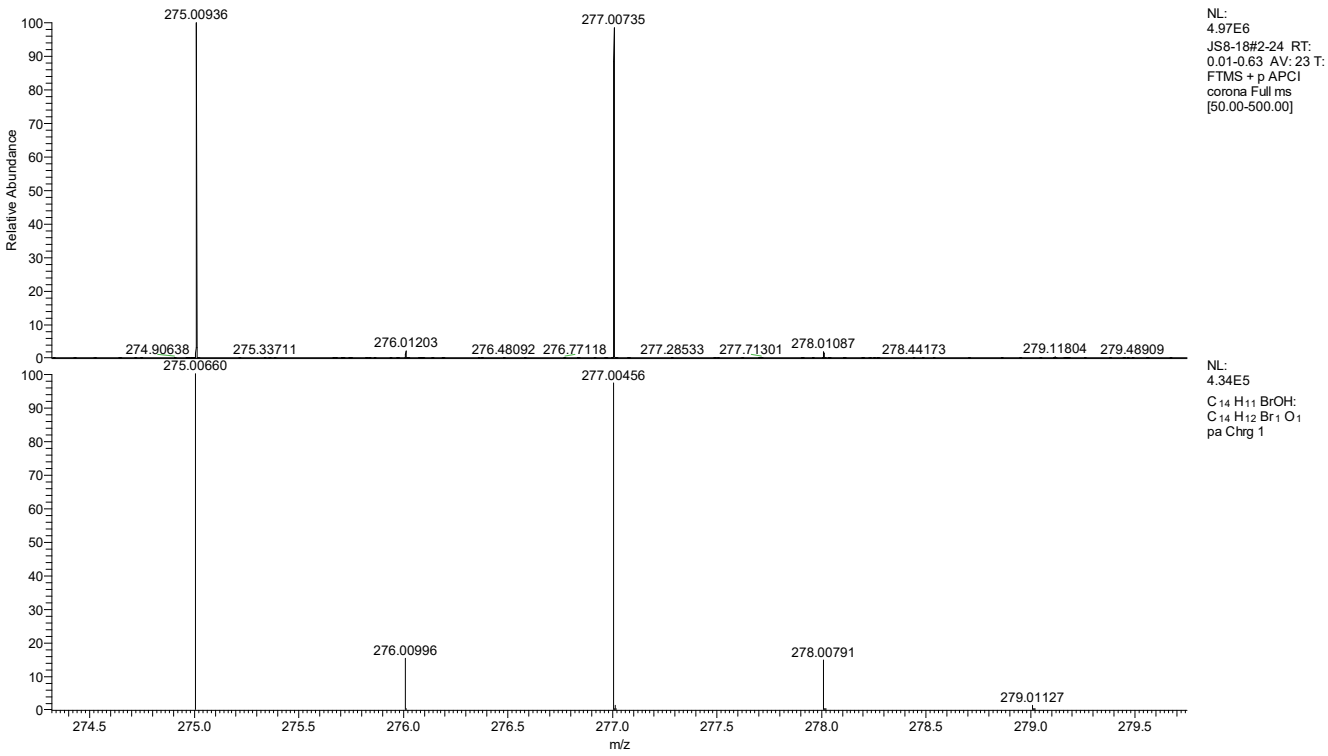


Figure S43. HRMS (ESI pos) spectra of **S6** (top:measured, bottom: calcd.).

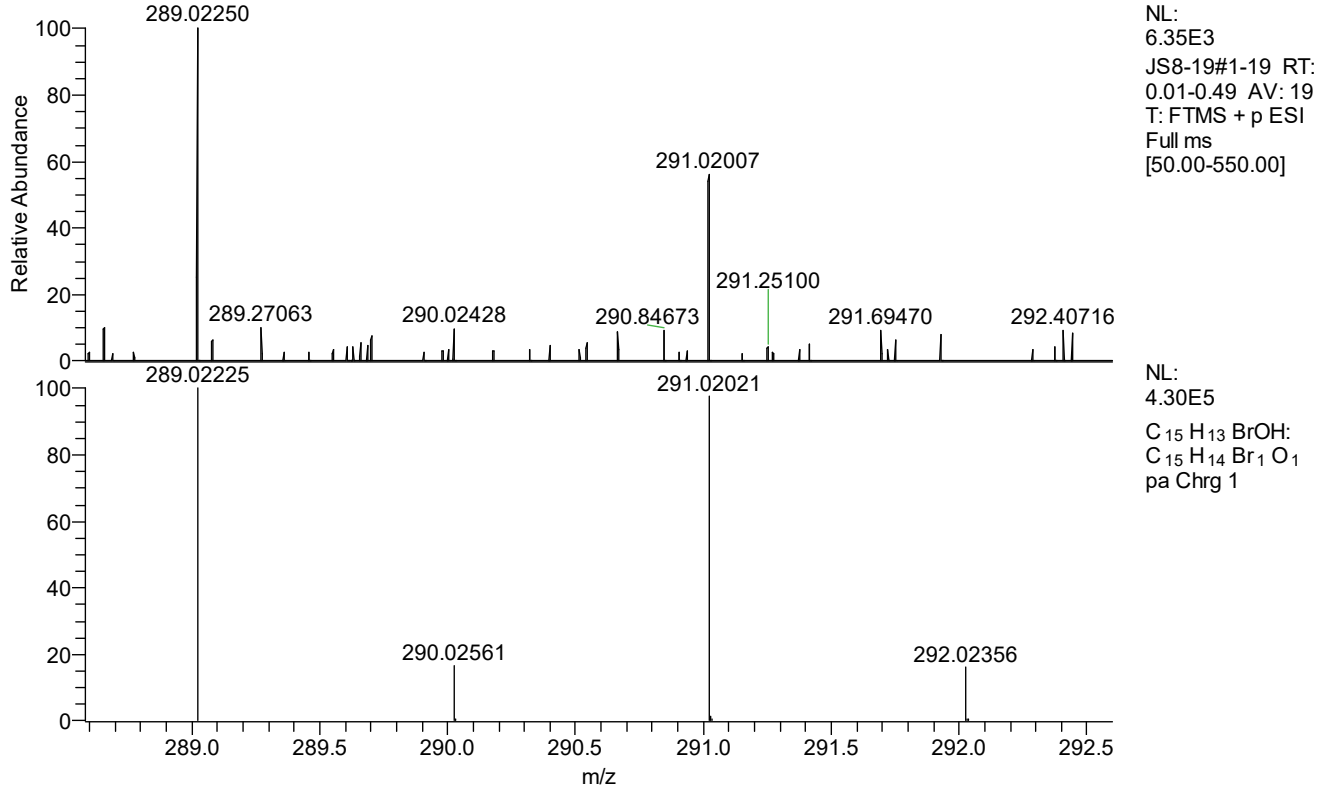


Figure S44. HRMS (ESI pos) spectra of **S7** (top:measured, bottom: calcd.).

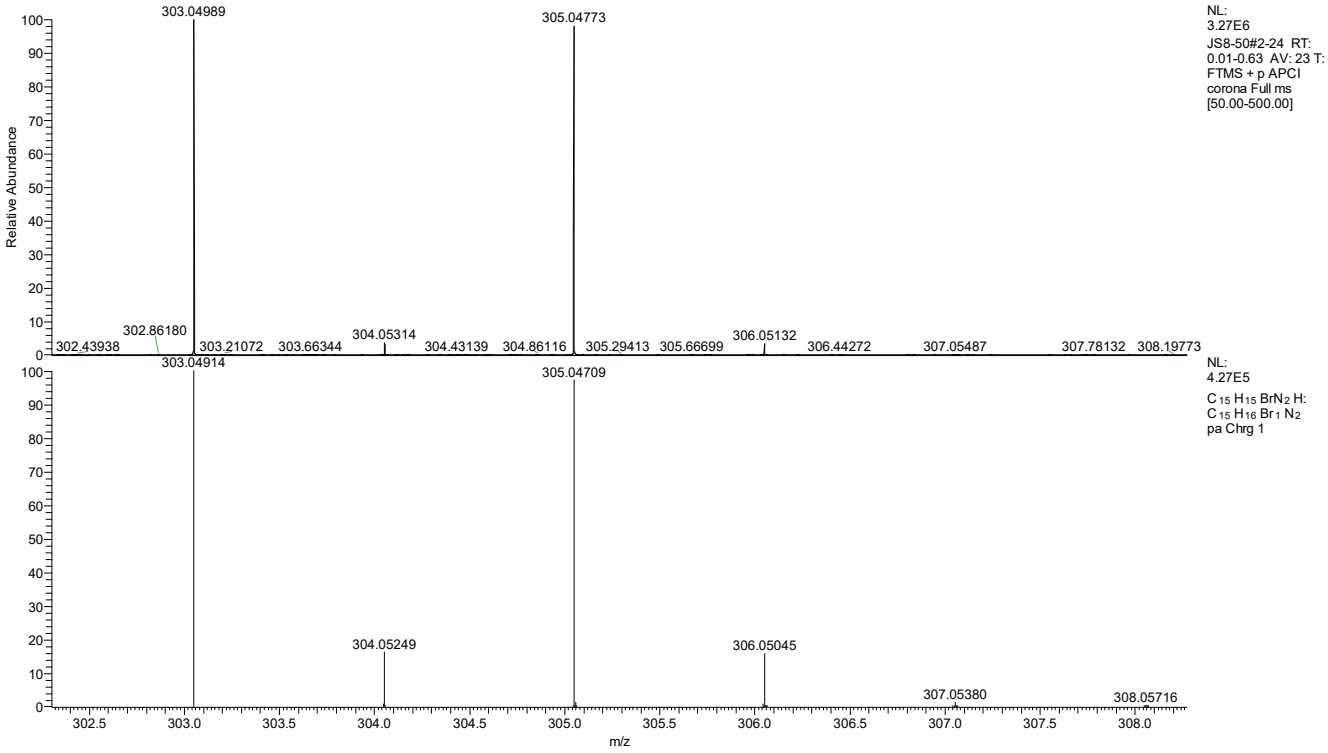


Figure S45. HRMS (ESI pos) spectra of **S8** (top:measured, bottom: calcd.).

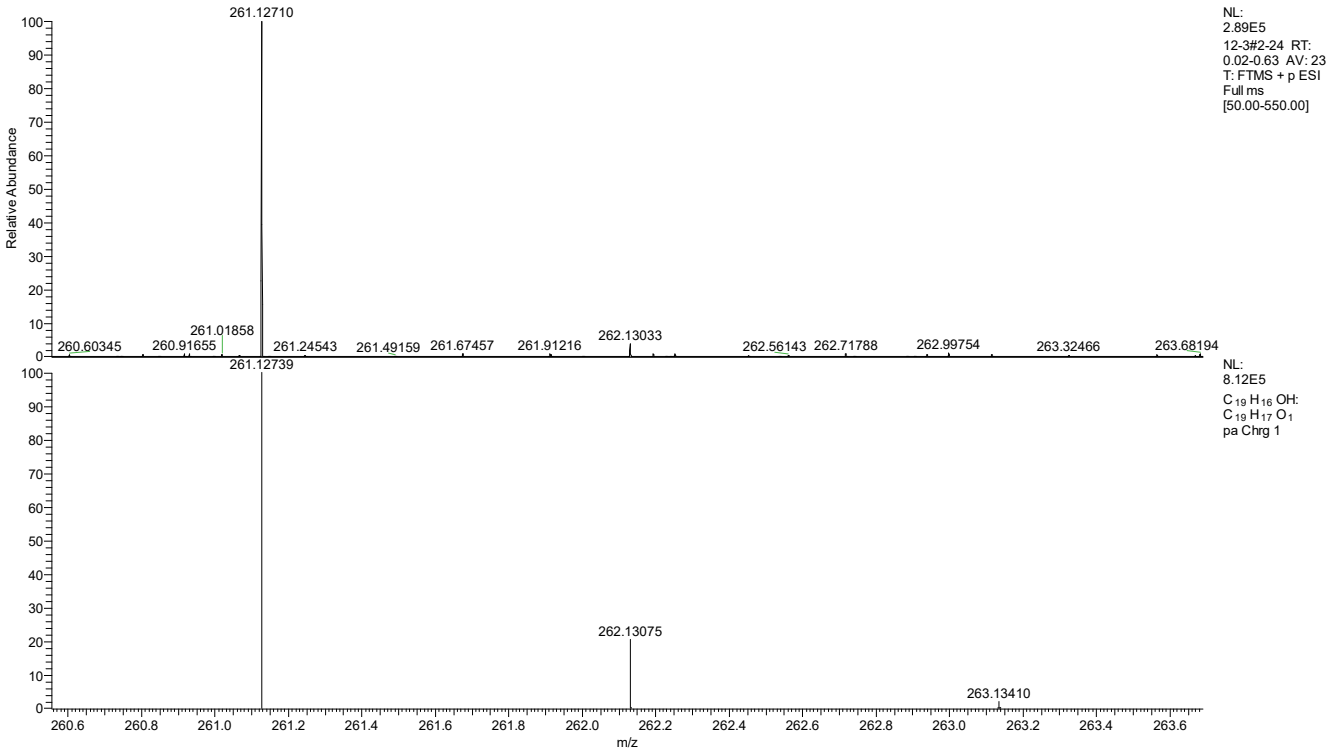


Figure S46. HRMS (ESI pos) spectra of **S11** (top:measured, bottom: calcd.).

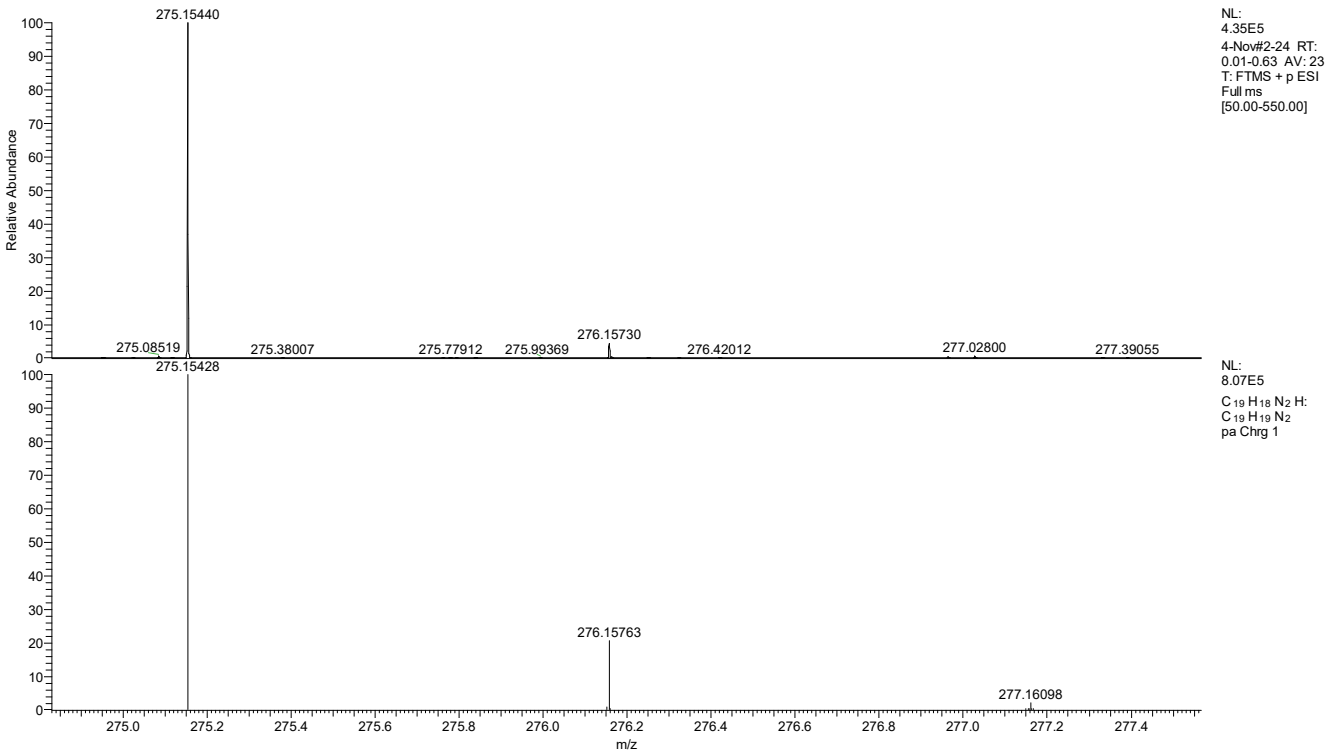
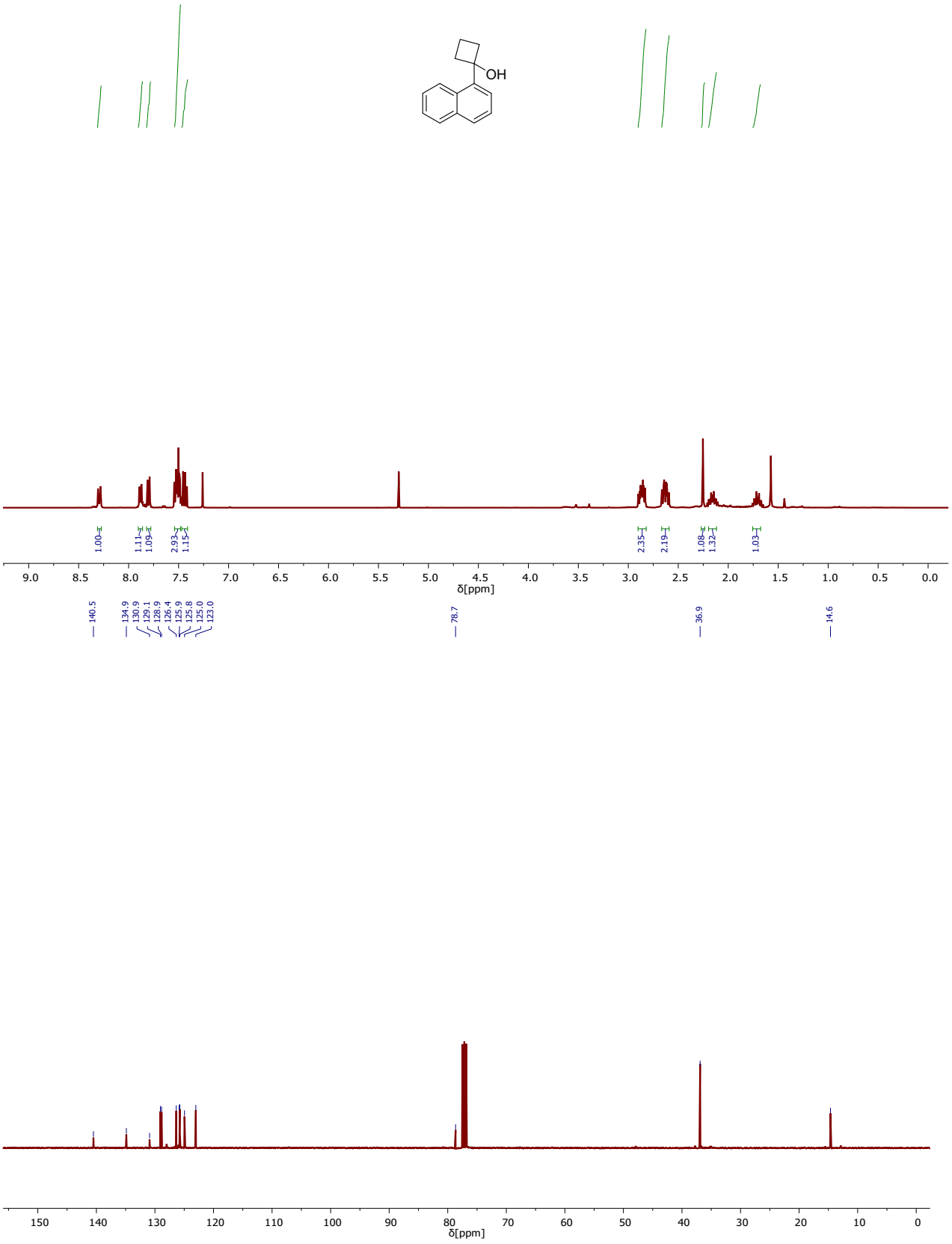
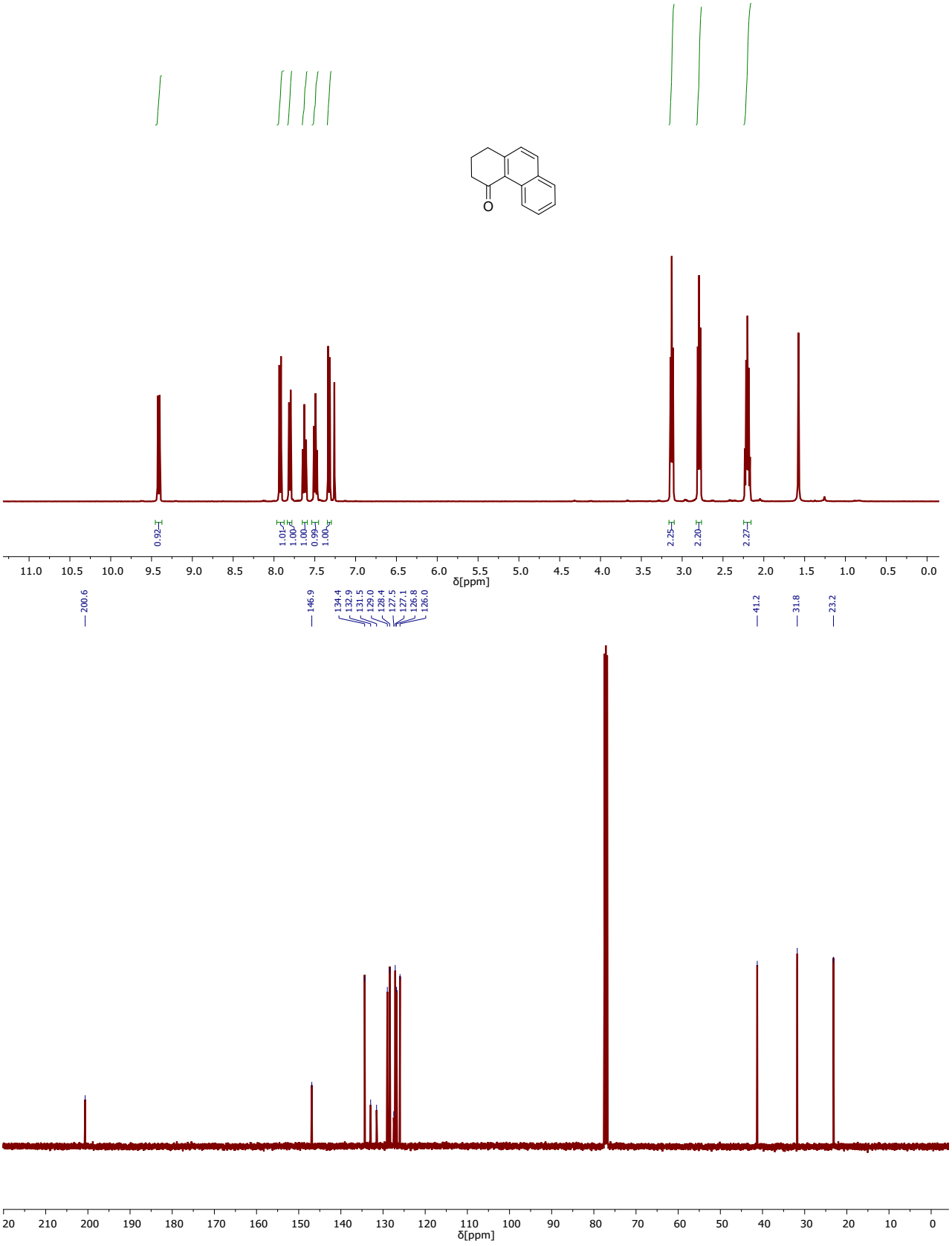


Figure S47. HRMS (ESI pos) spectra of **S12** (top:measured, bottom: calcd.).

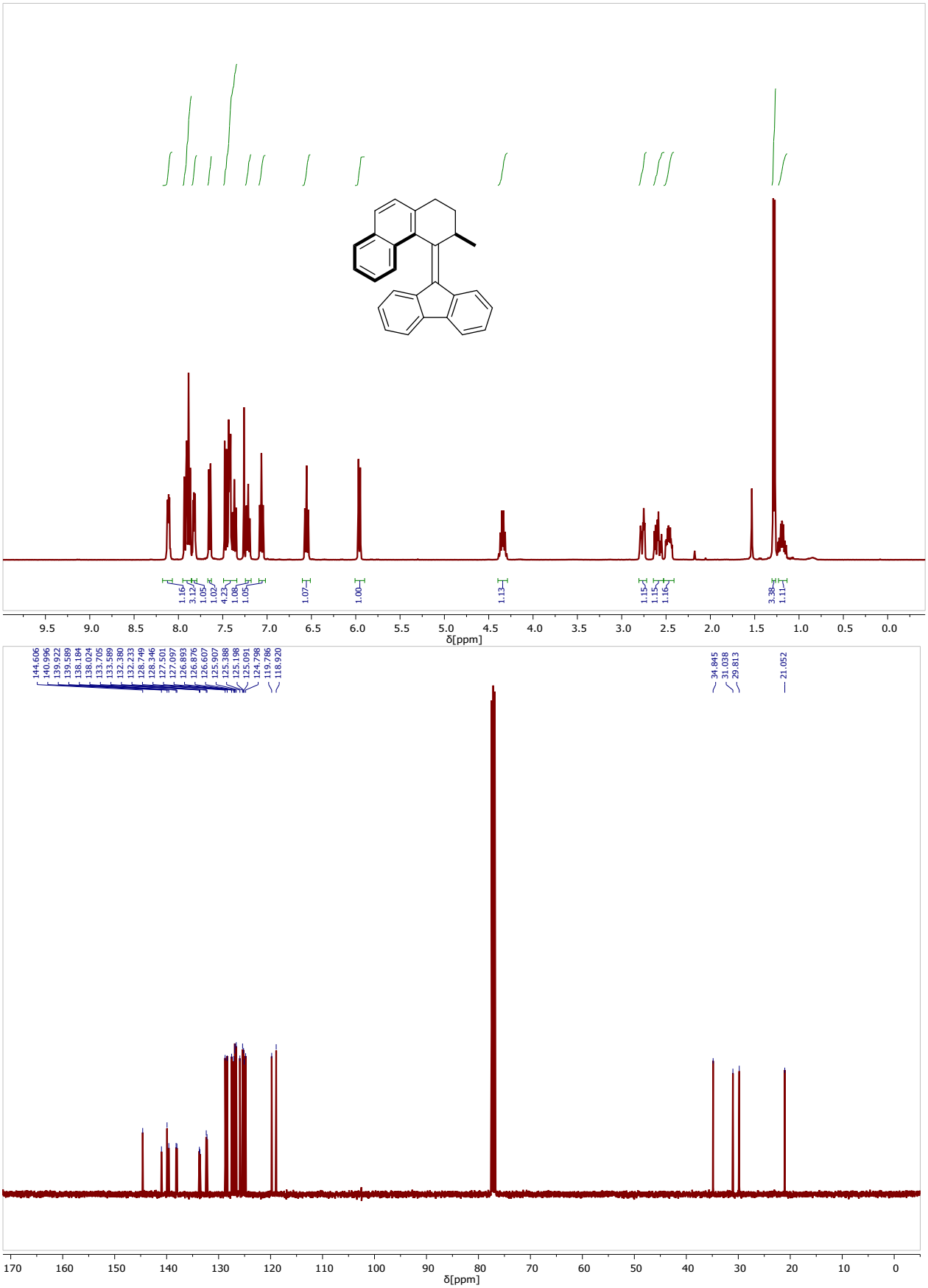
NMR spectra



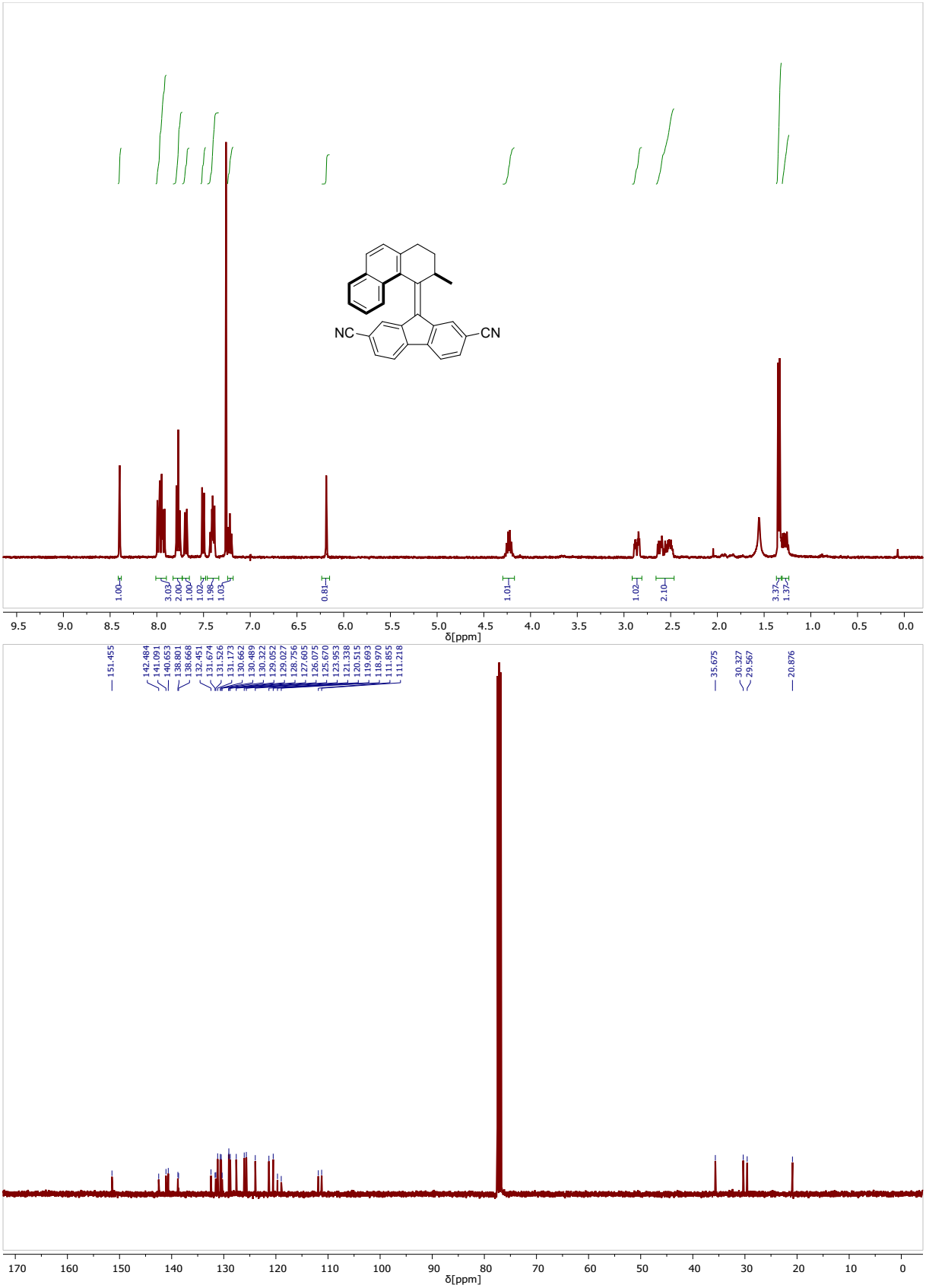
^{1}H NMR and ^{13}C NMR of compound S**1**.



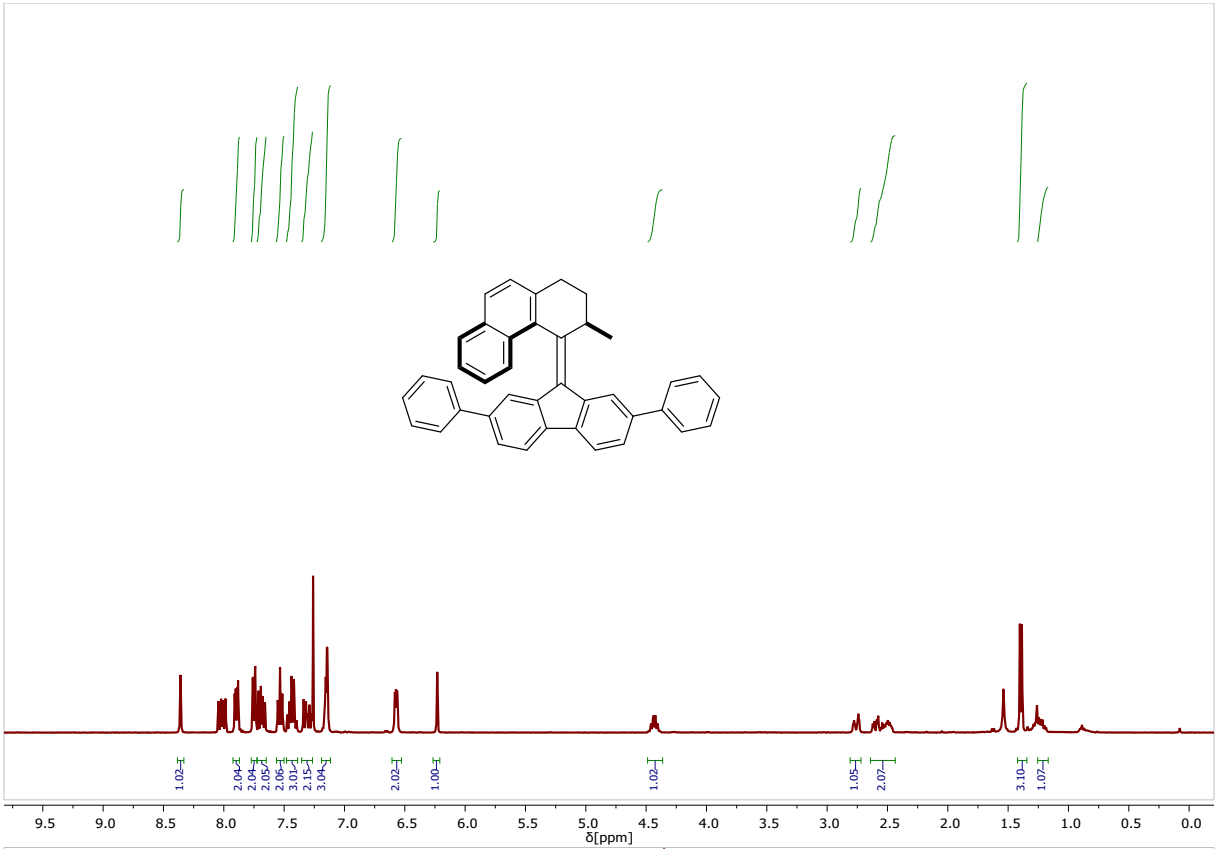
^{1}H NMR and ^{13}C NMR of compound S**2**.

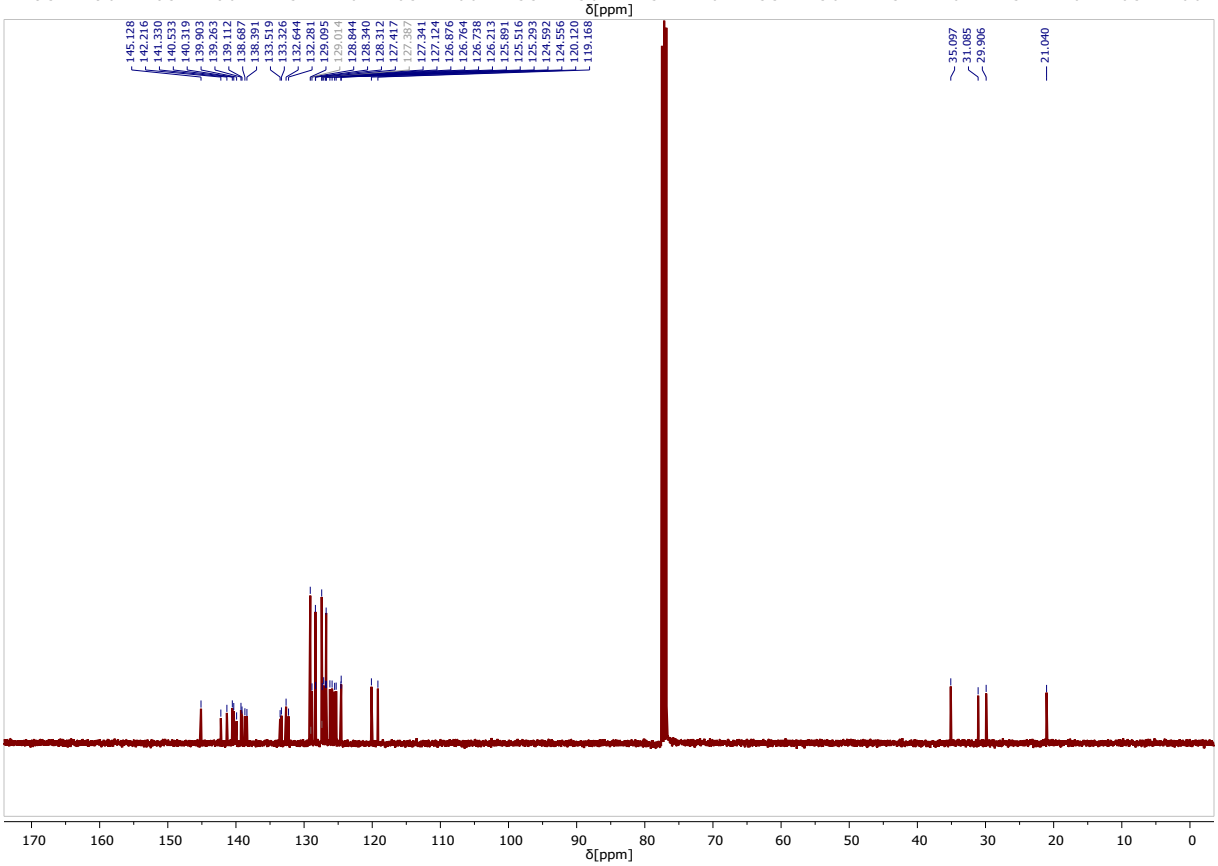


^{1}H NMR and ^{13}C NMR of compound **1**.

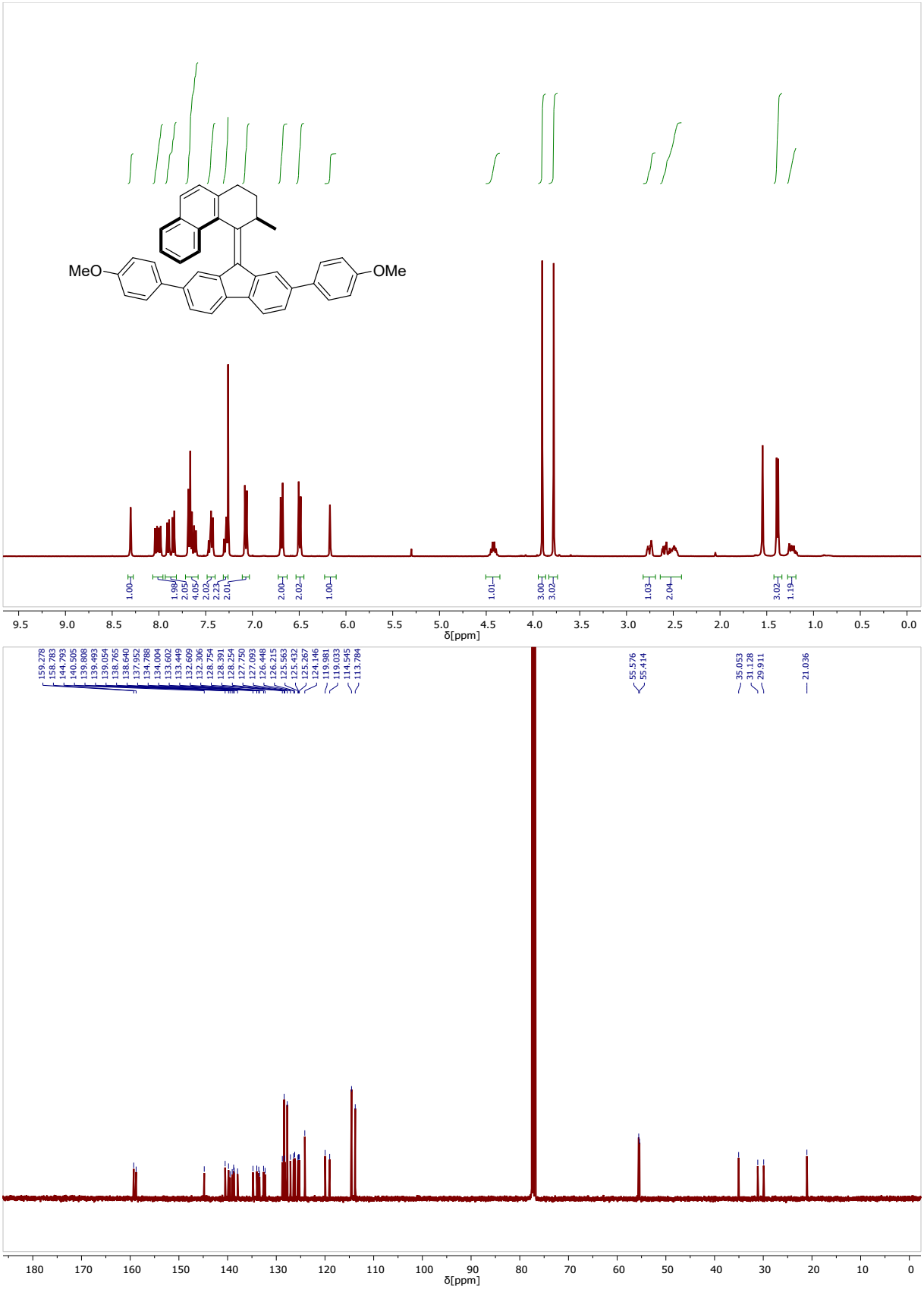


^{1}H NMR and ^{13}C NMR of compound **3**.

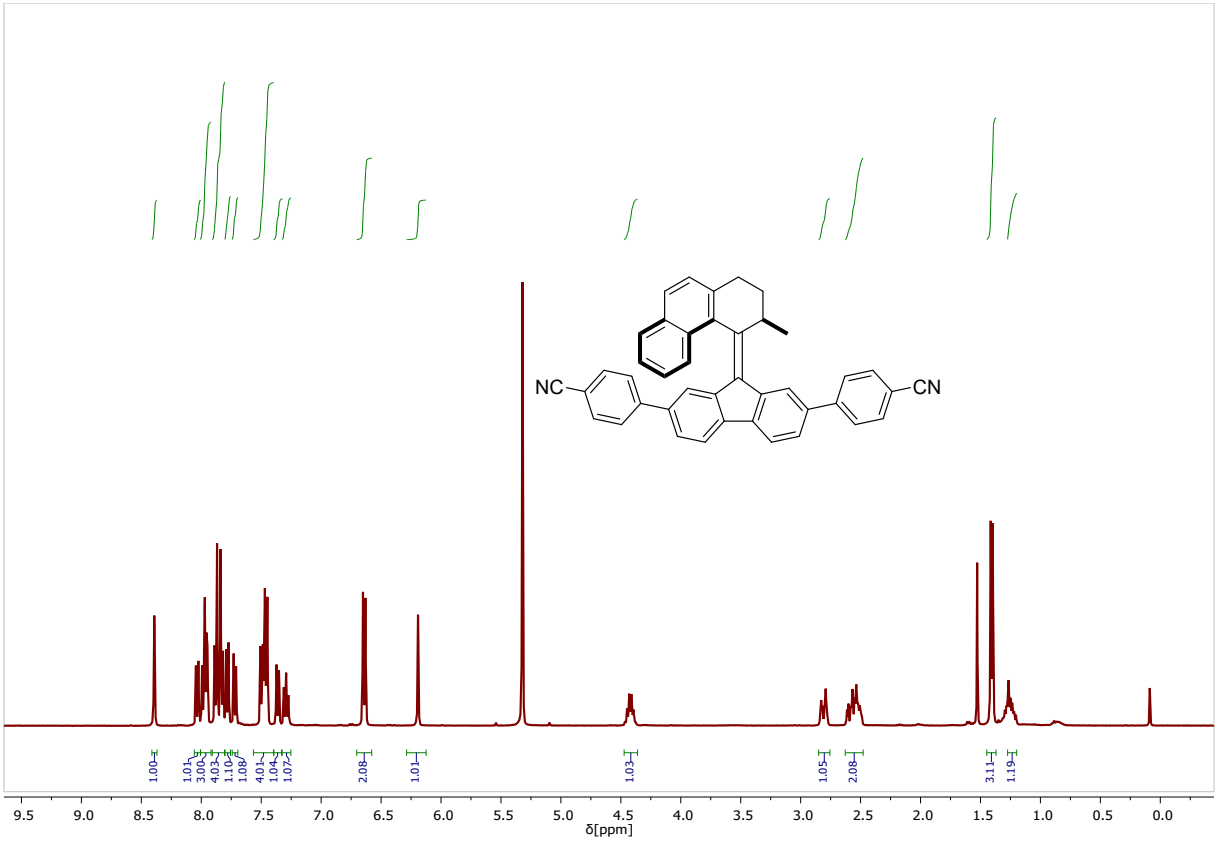


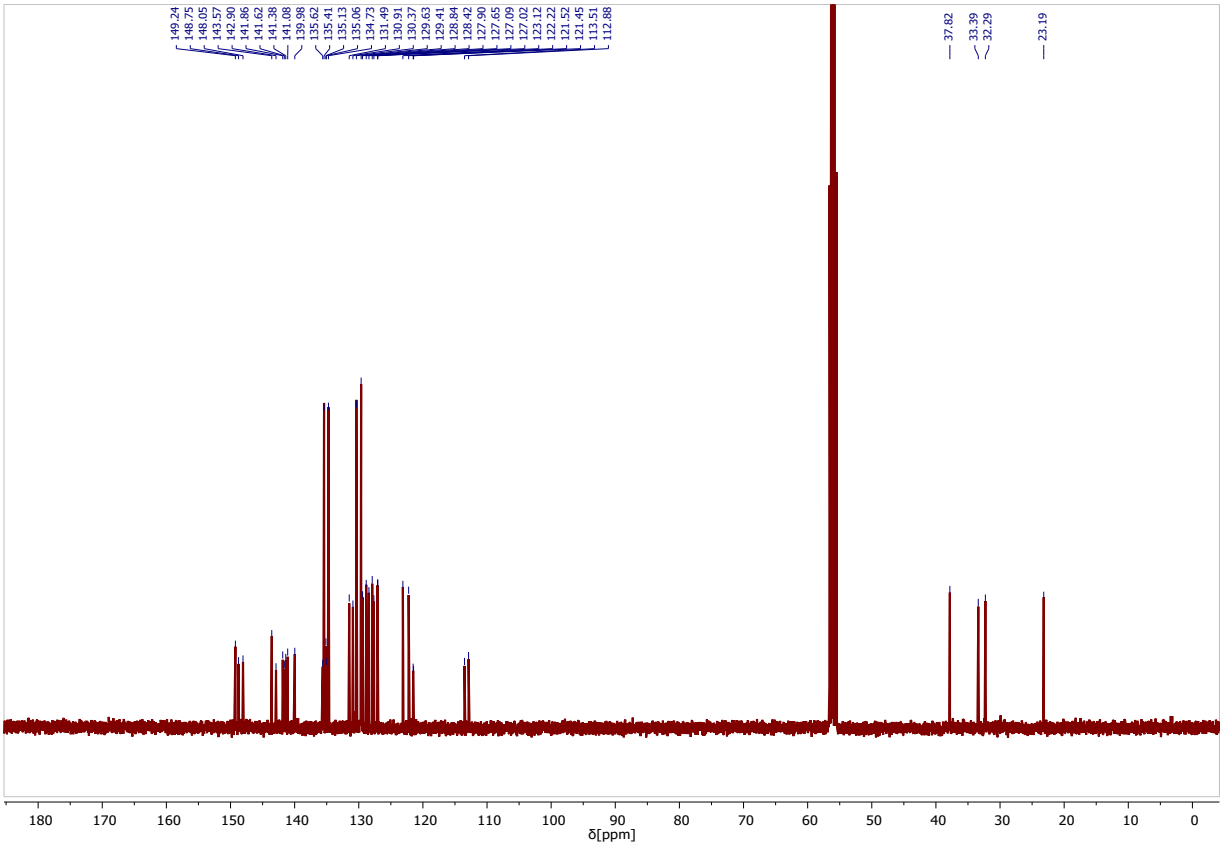


^{1}H NMR and ^{13}C NMR of compound **4**.

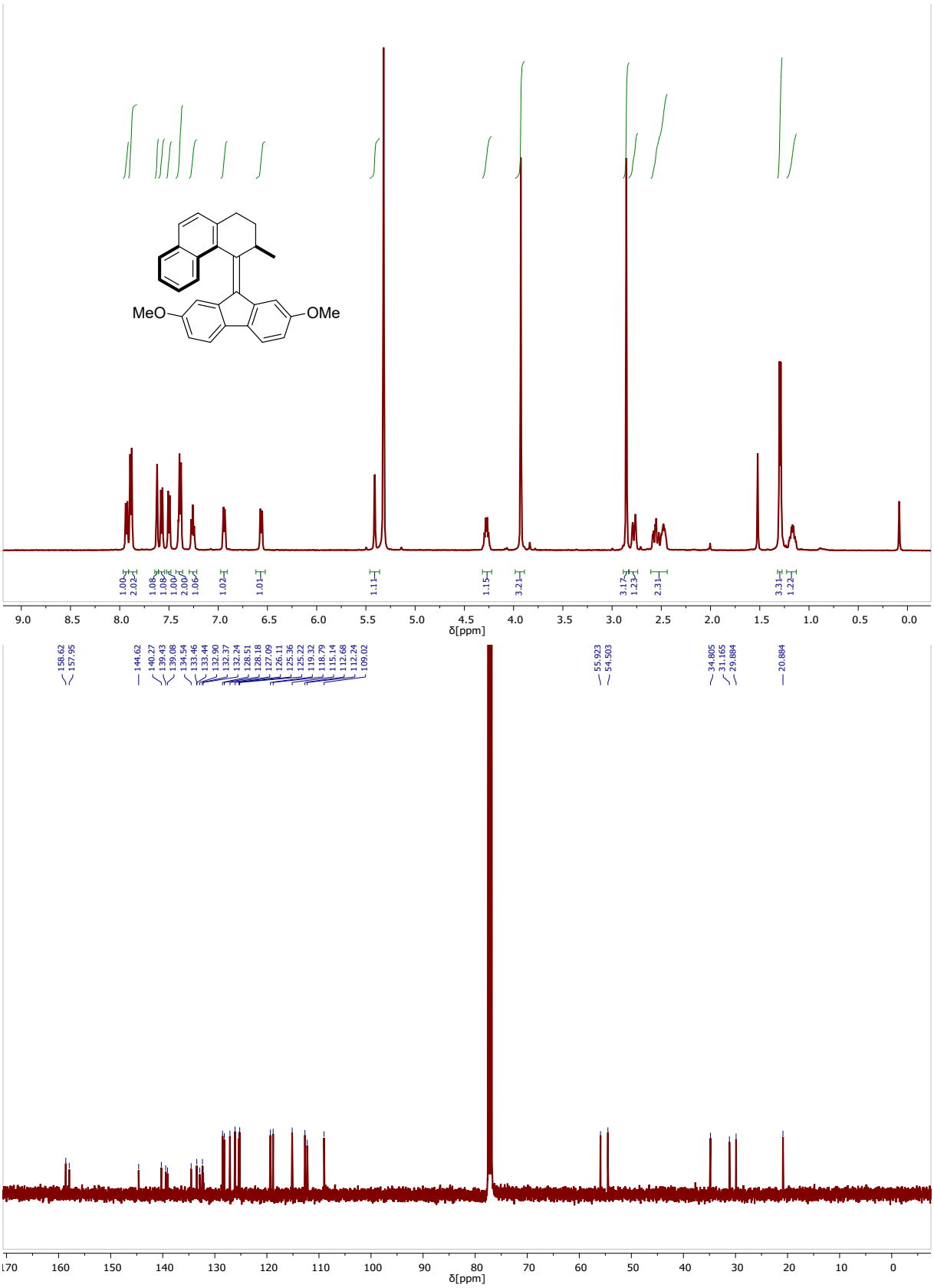


^{1}H NMR and ^{13}C NMR of compound **5**.

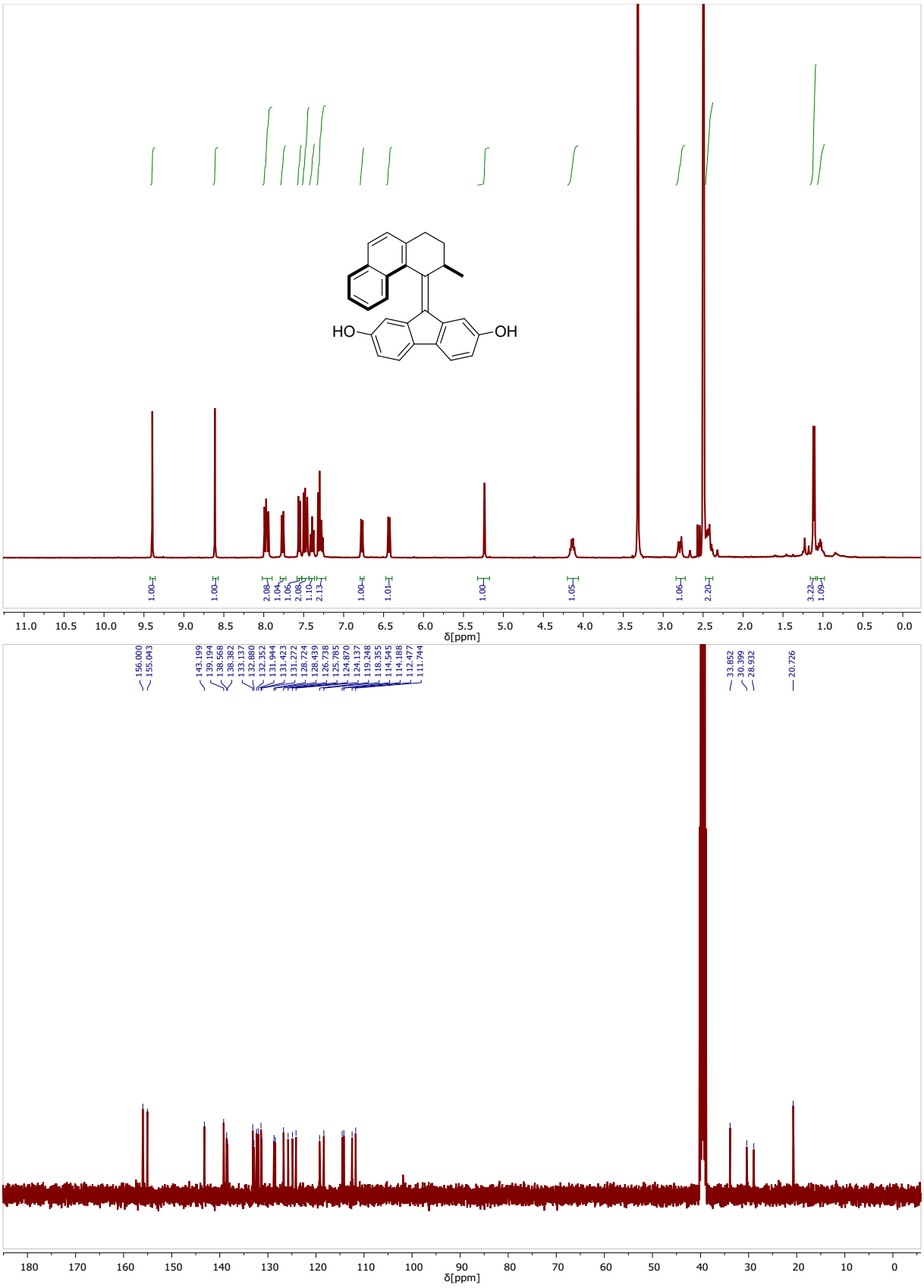




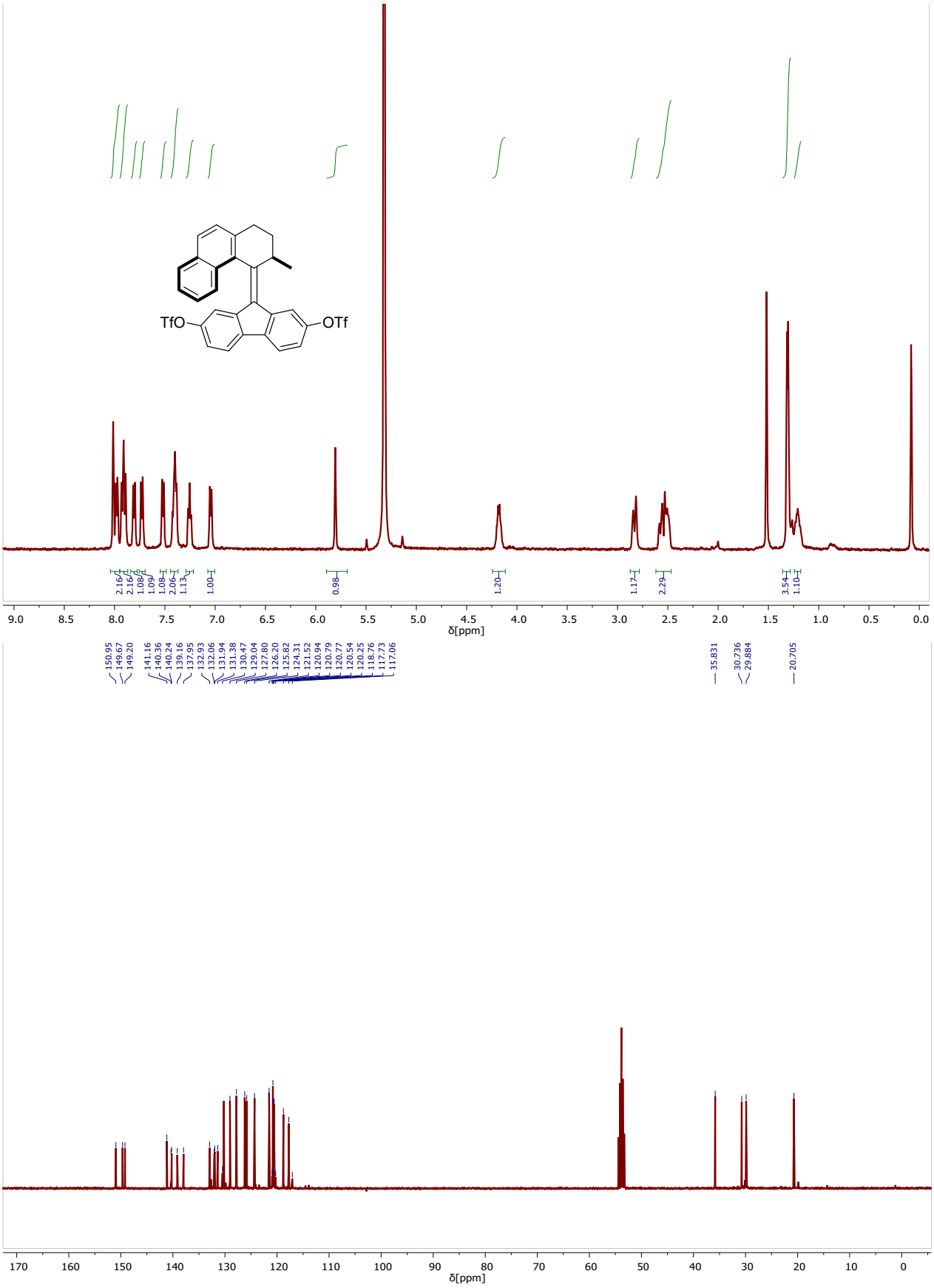
^{1}H NMR and ^{13}C NMR of compound **6**.



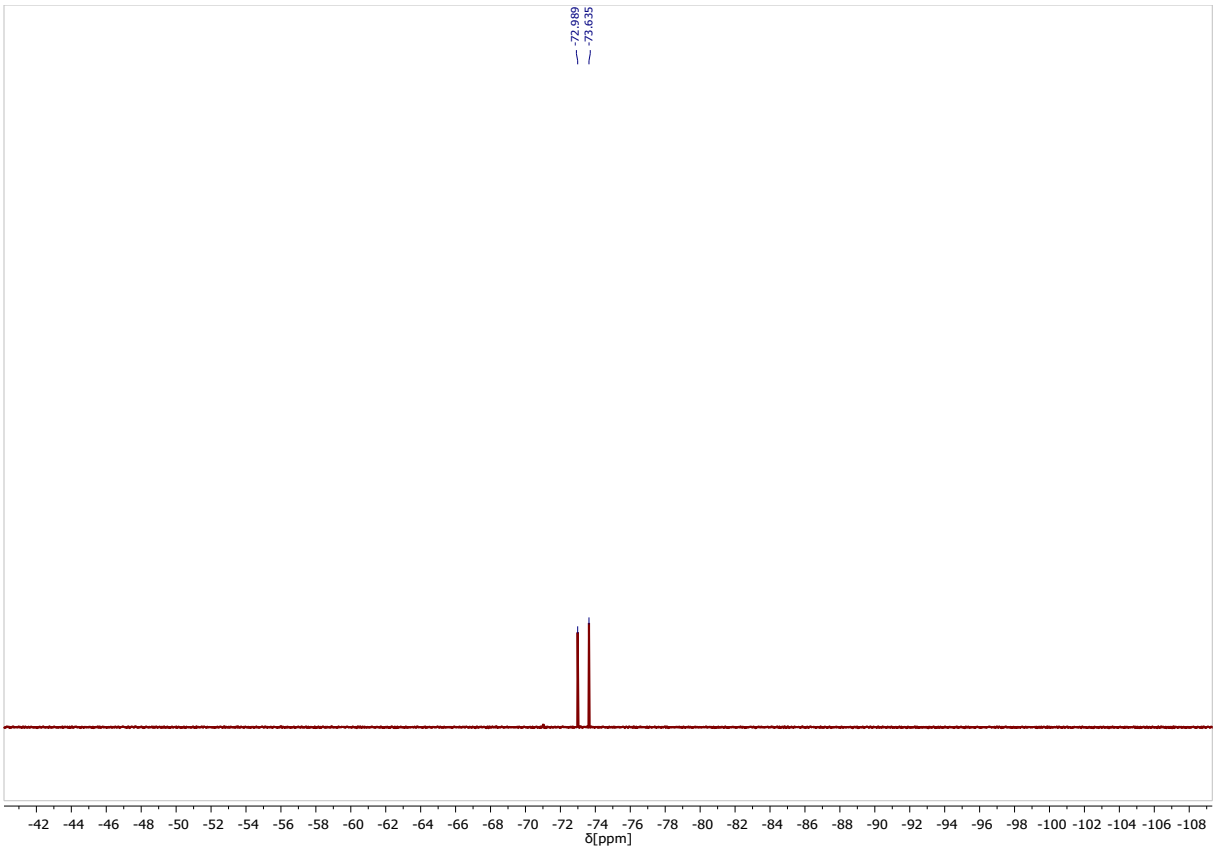
^{1}H NMR and ^{13}C NMR of compound **7**.



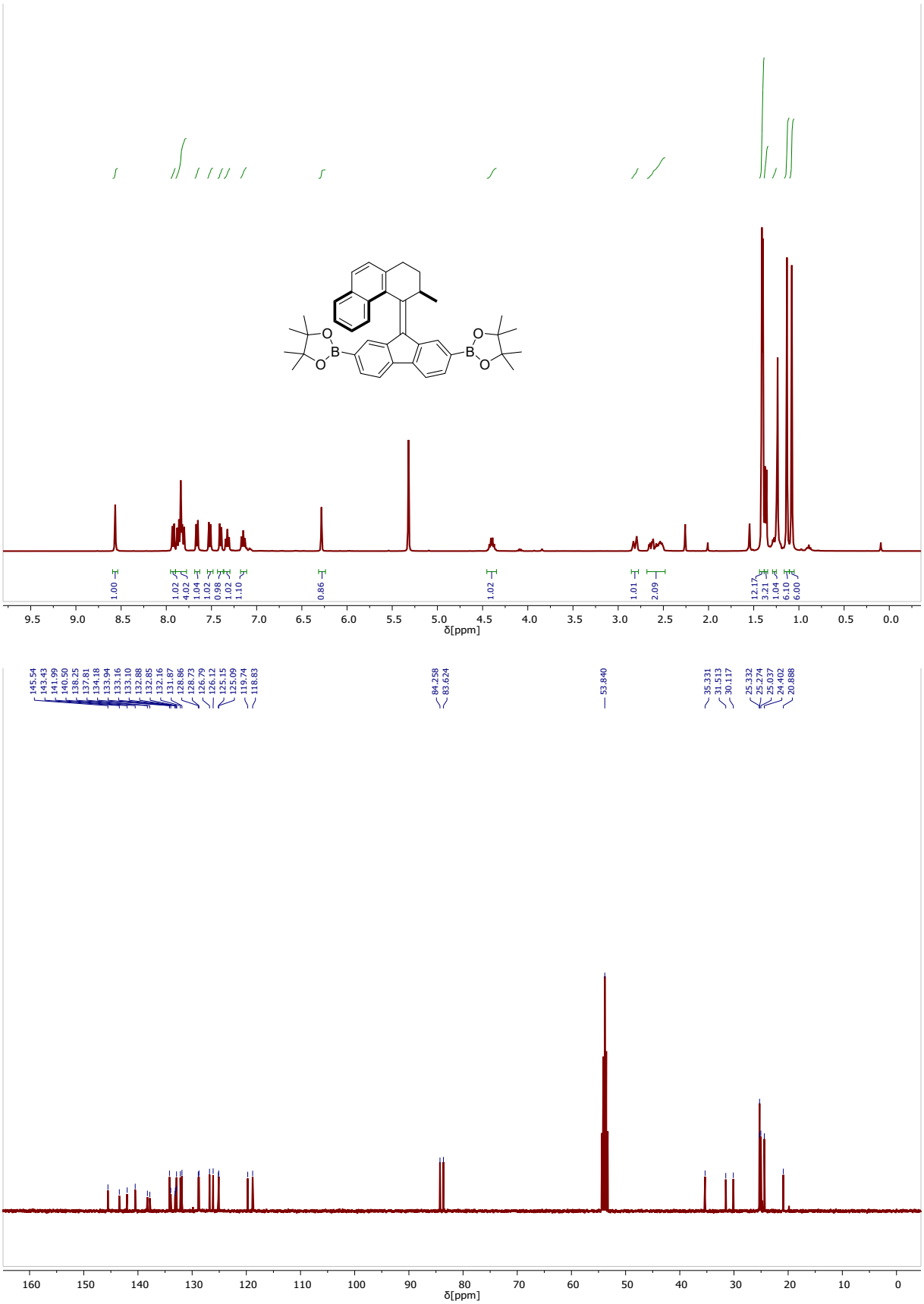
^{1}H NMR and ^{13}C NMR of compound **7'**.



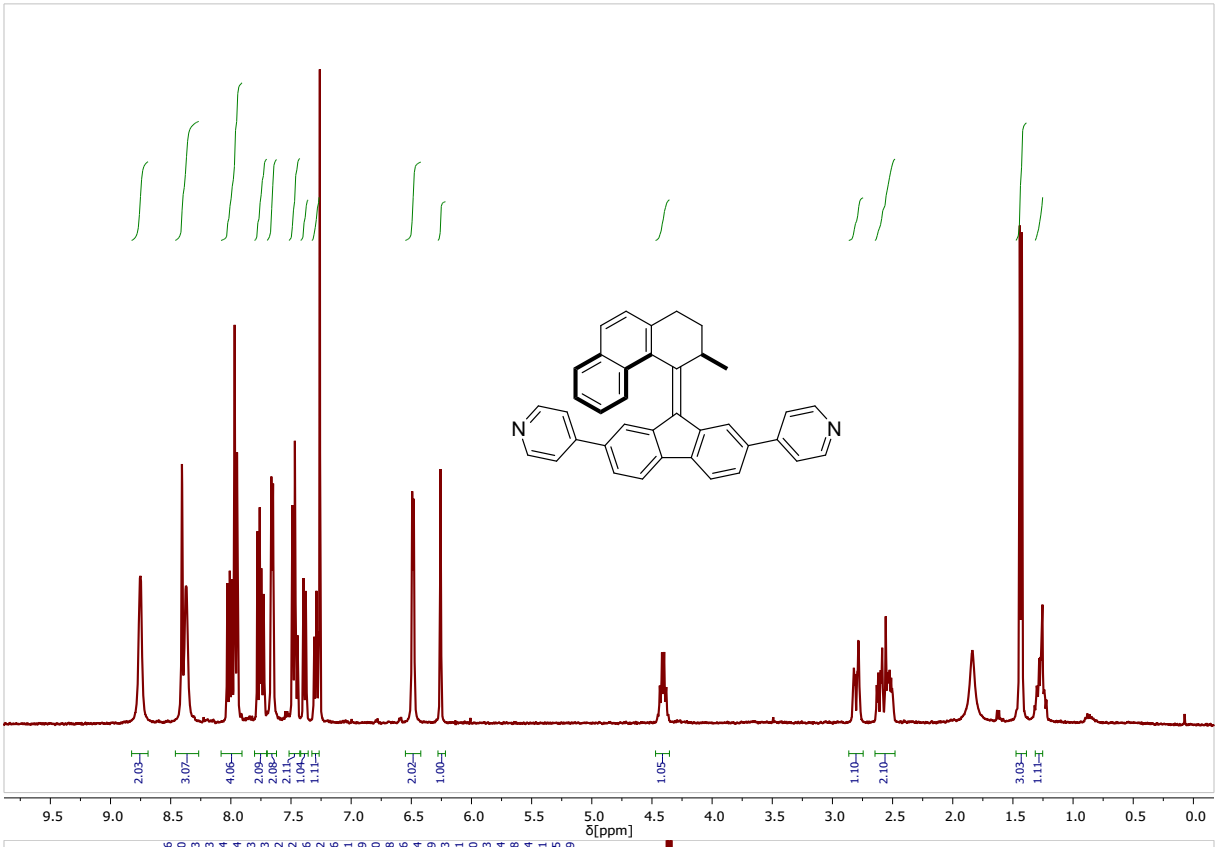
^{1}H NMR and ^{13}C NMR of compound **8**.

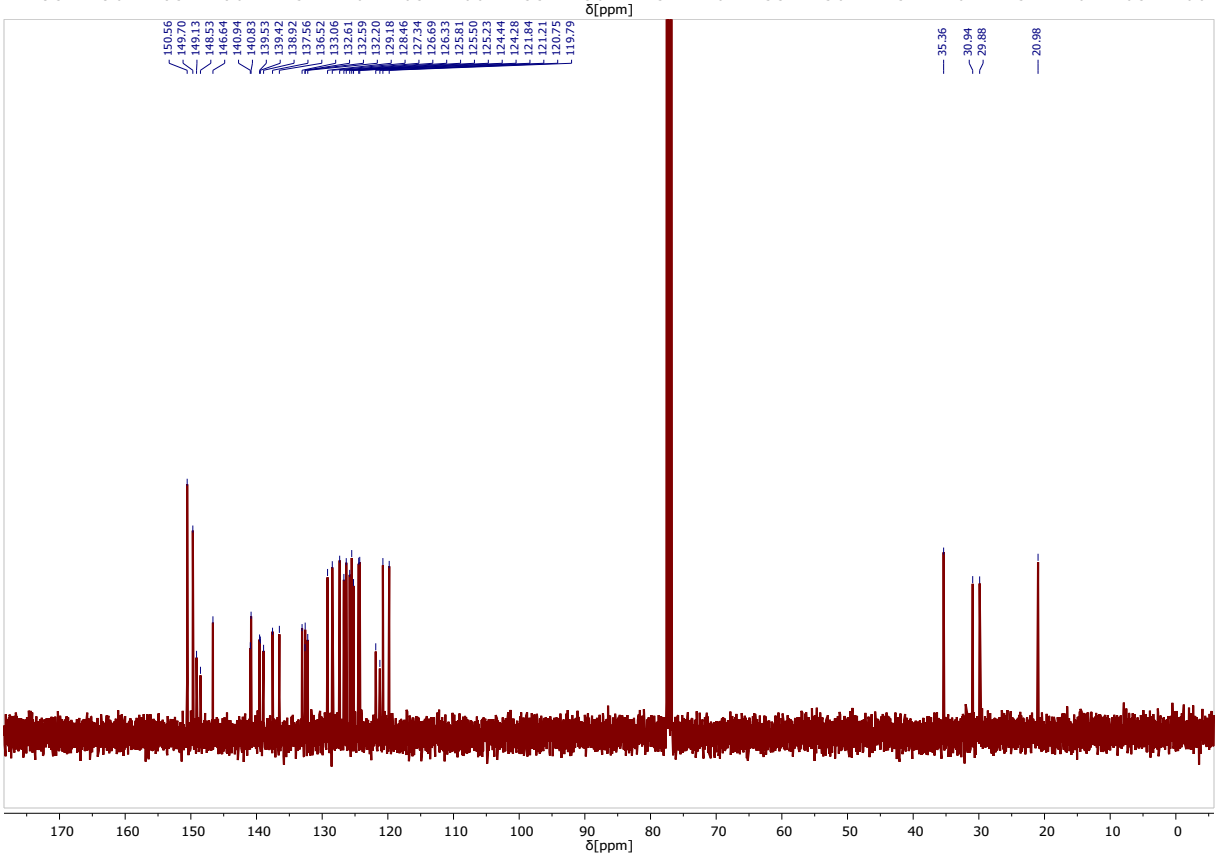


^{19}F NMR of compound **8**.

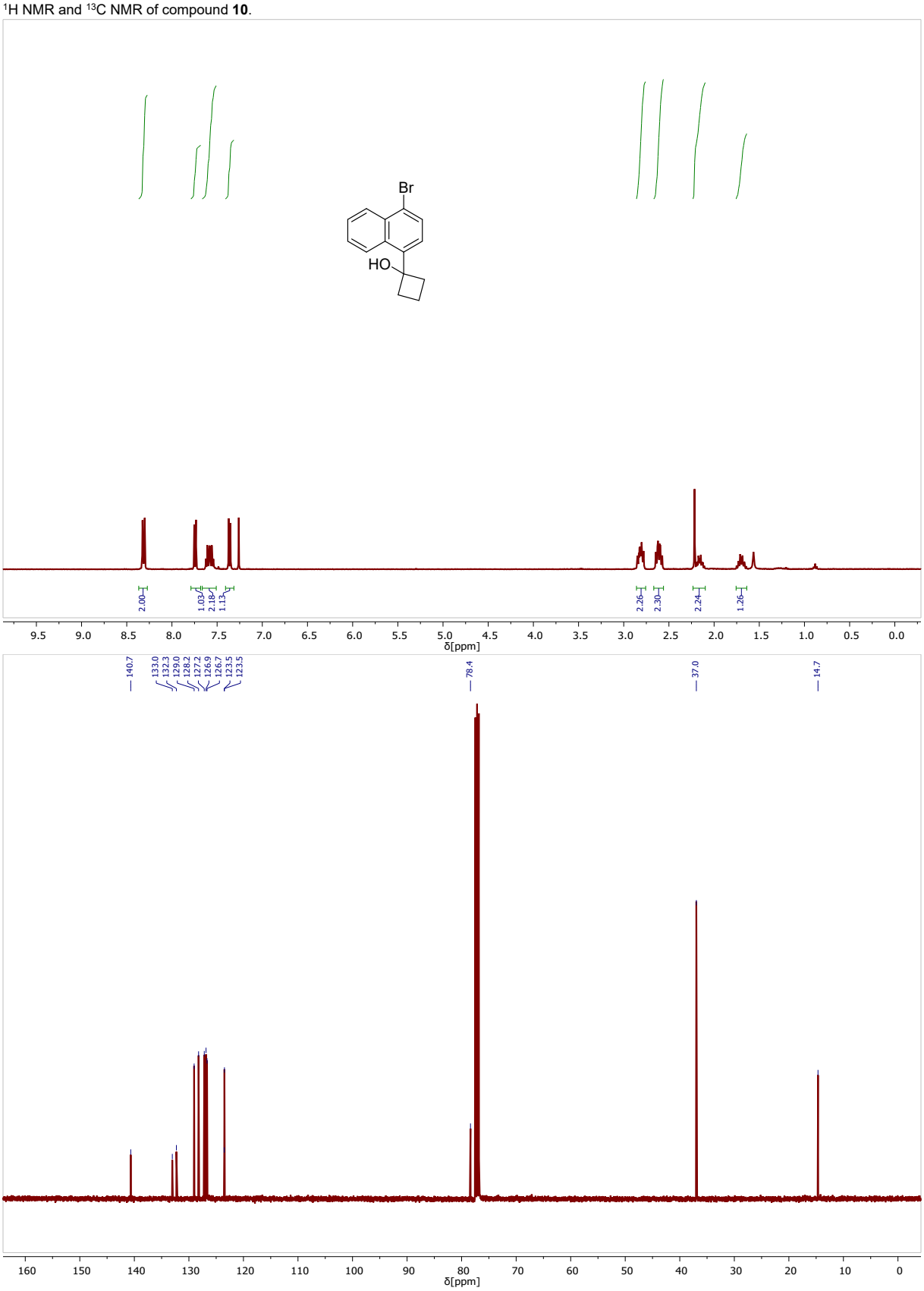


^{1}H NMR and ^{13}C NMR of compound **9**.

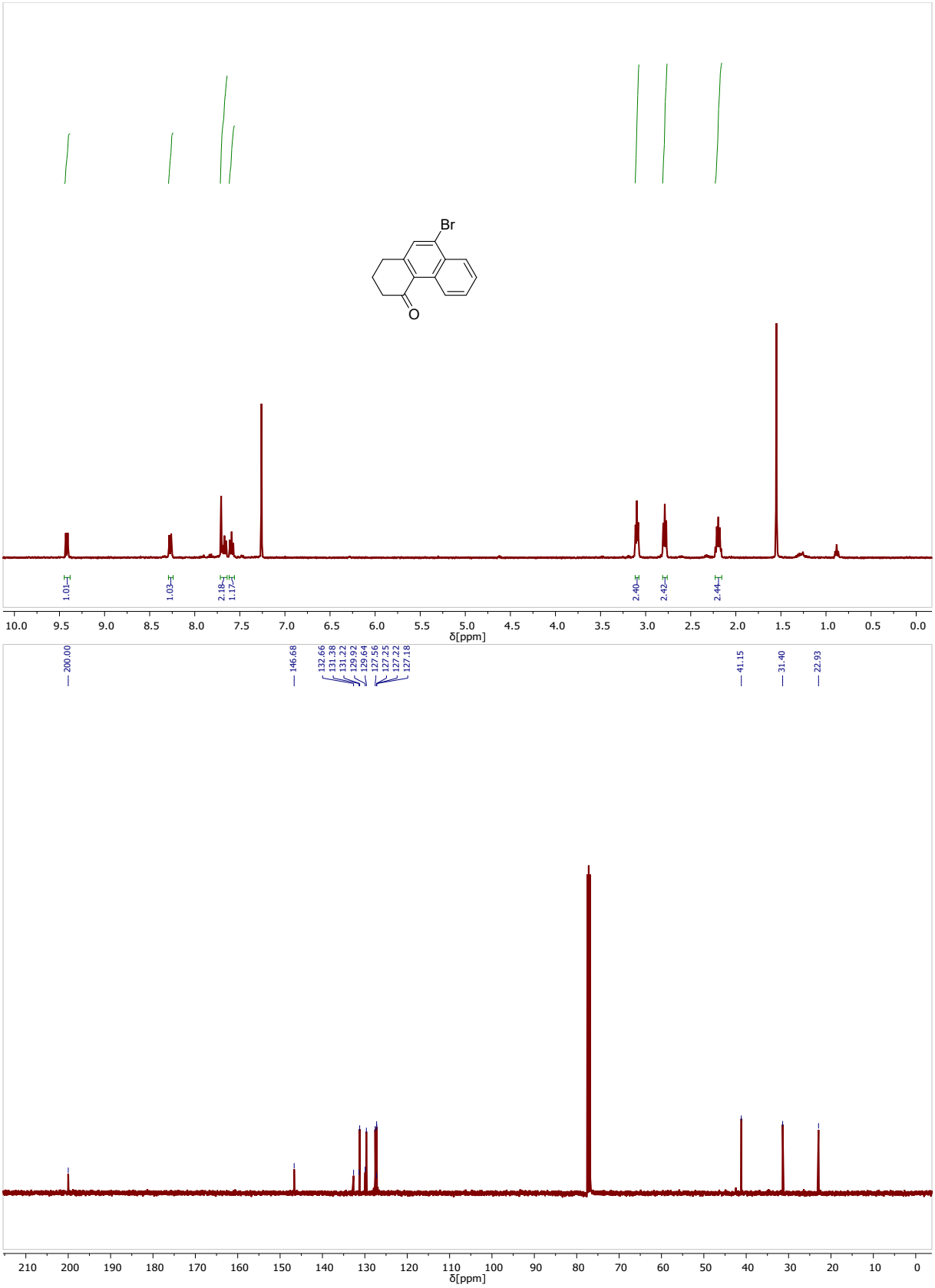

N
N
2.03
3.07
4.06
2.09
2.08
2.11
1.04
1.11
2.02
1.00
1.05
1.10
2.10
3.03
1.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ[ppm]


150.56
149.70
149.13
148.53
146.64
140.94
140.83
139.53
139.42
138.92
137.56
136.52
133.06
132.61
132.59
132.20
129.18
128.46
127.34
126.69
126.33
125.81
125.50
125.23
124.44
124.28
121.84
121.71
120.75
119.79
35.36
30.94
29.88
20.98
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
δ[ppm]

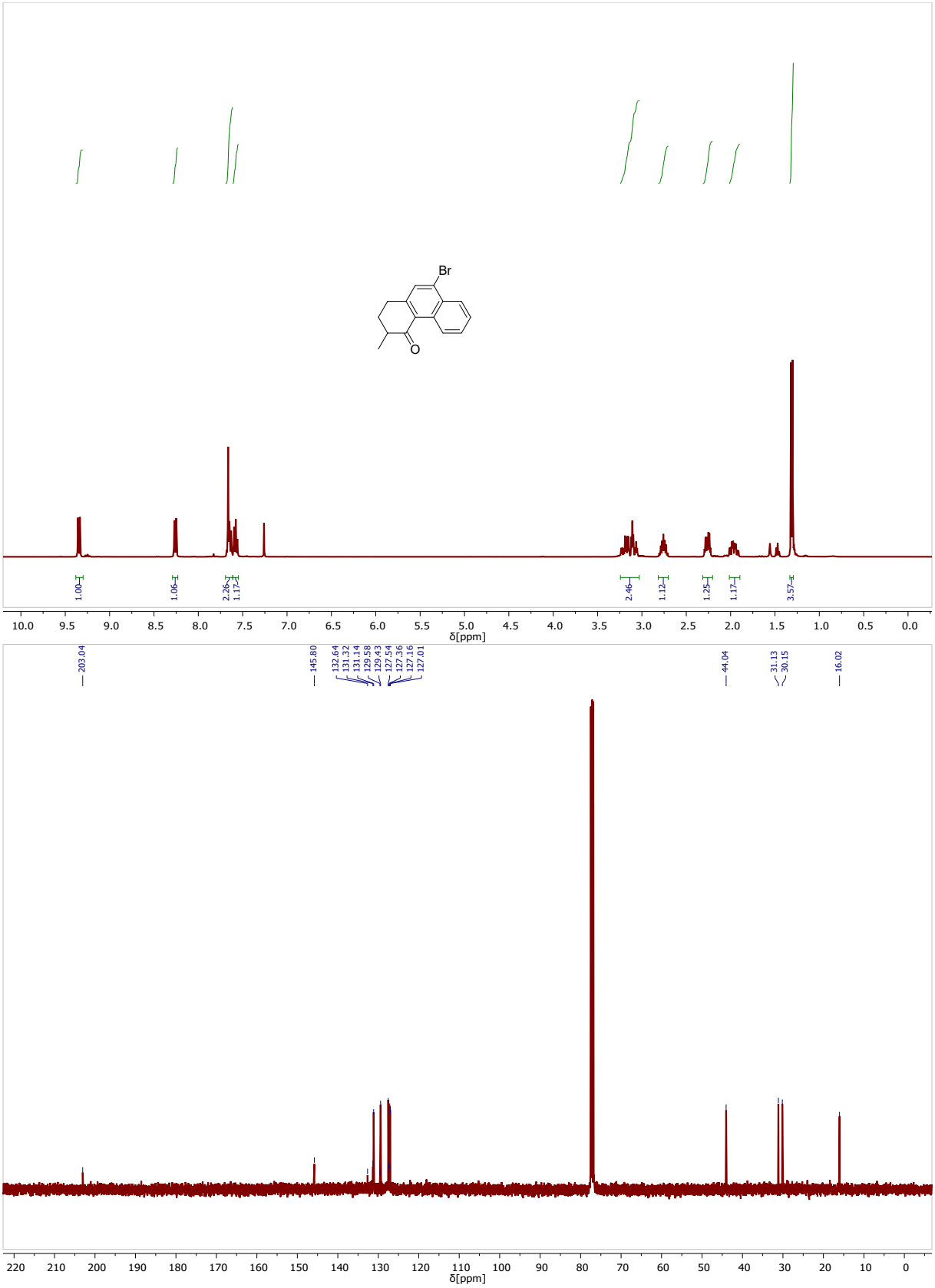
^{1}H NMR and ^{13}C NMR of compound **10**.



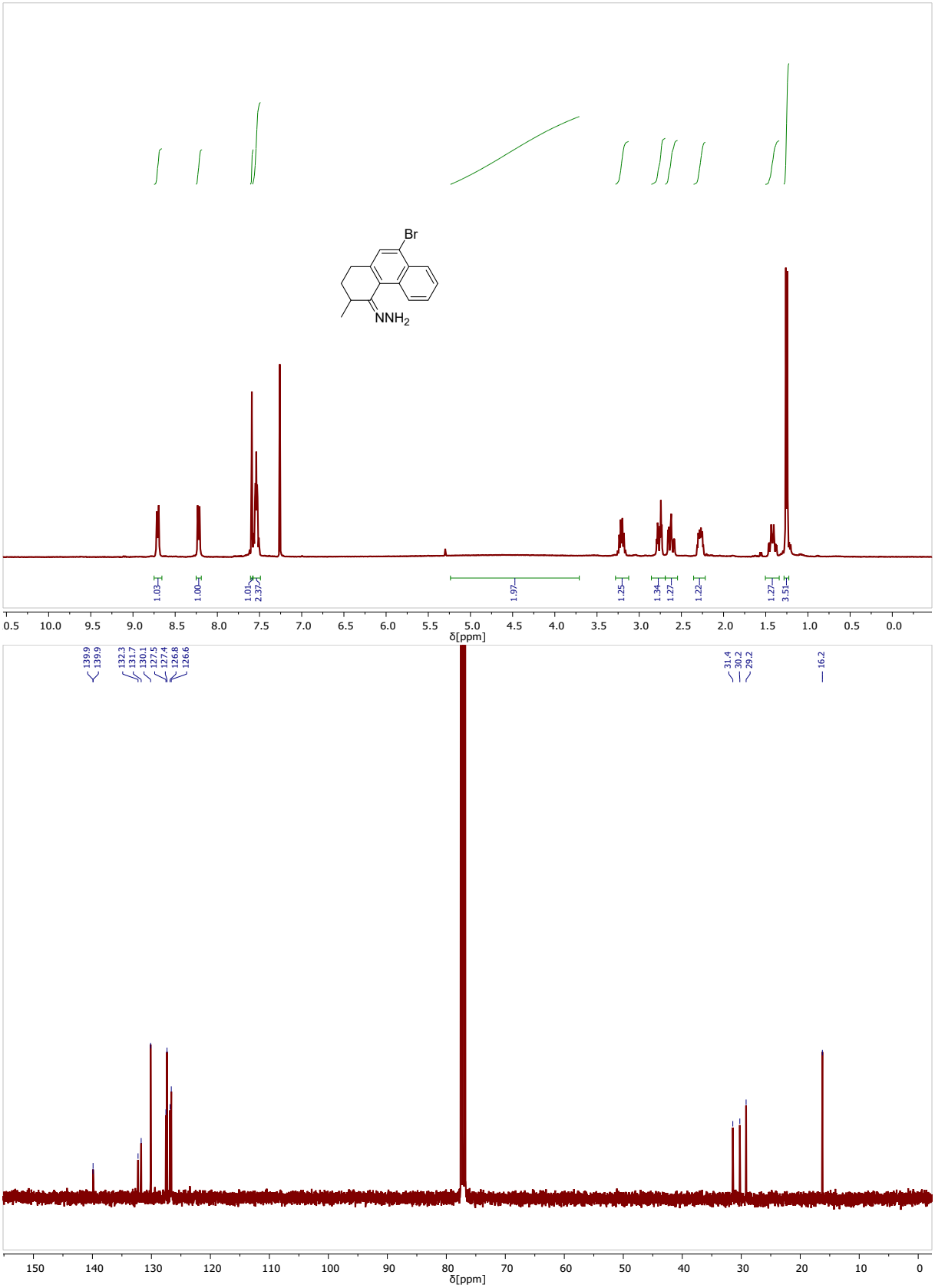
^{1}H NMR and ^{13}C NMR of compound **S5**.



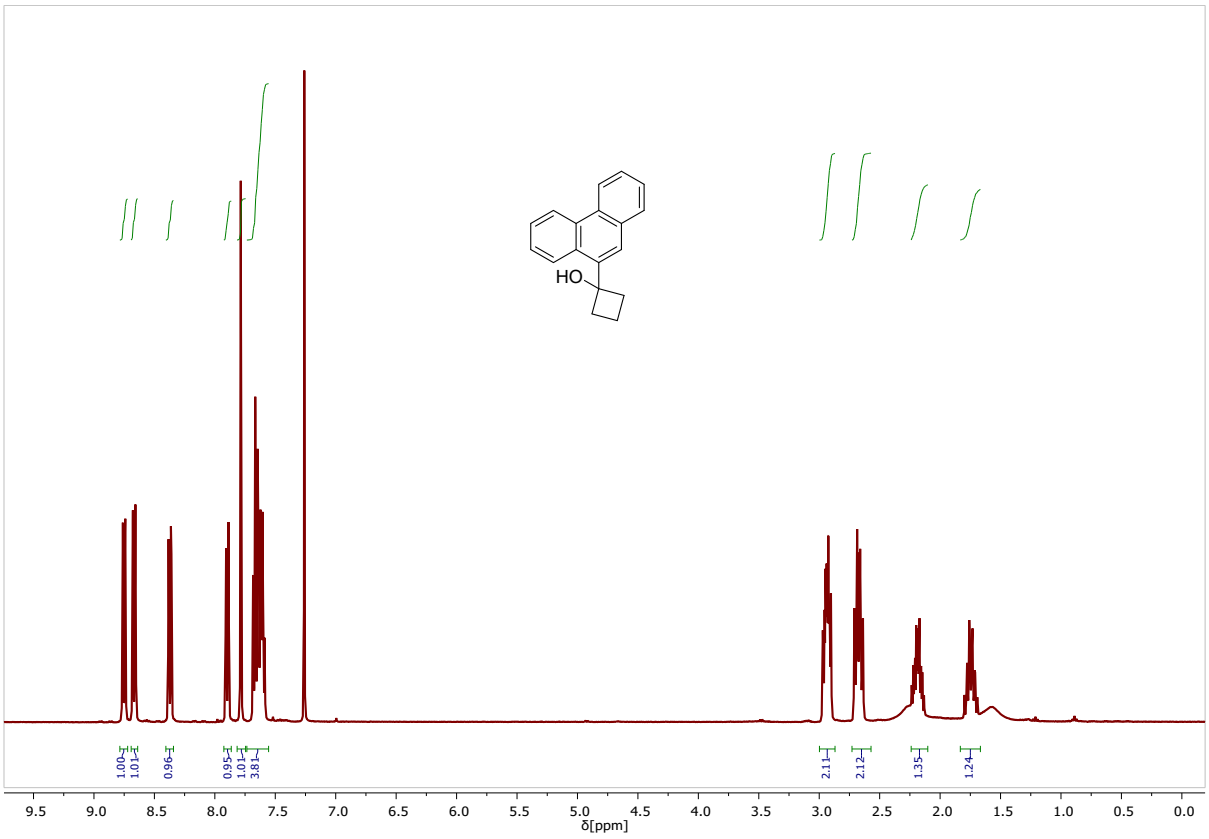
^{1}H NMR and ^{13}C NMR of compound **S6**.



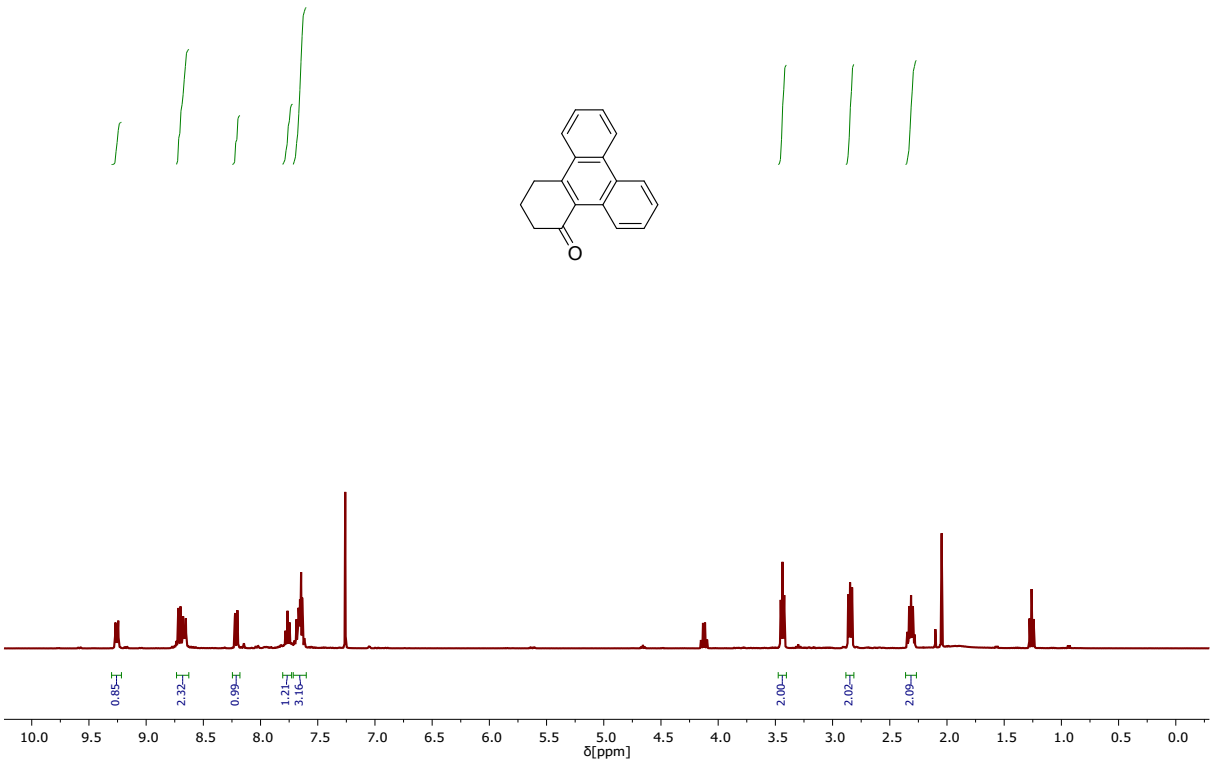
^{1}H NMR and ^{13}C NMR of compound **S7**.



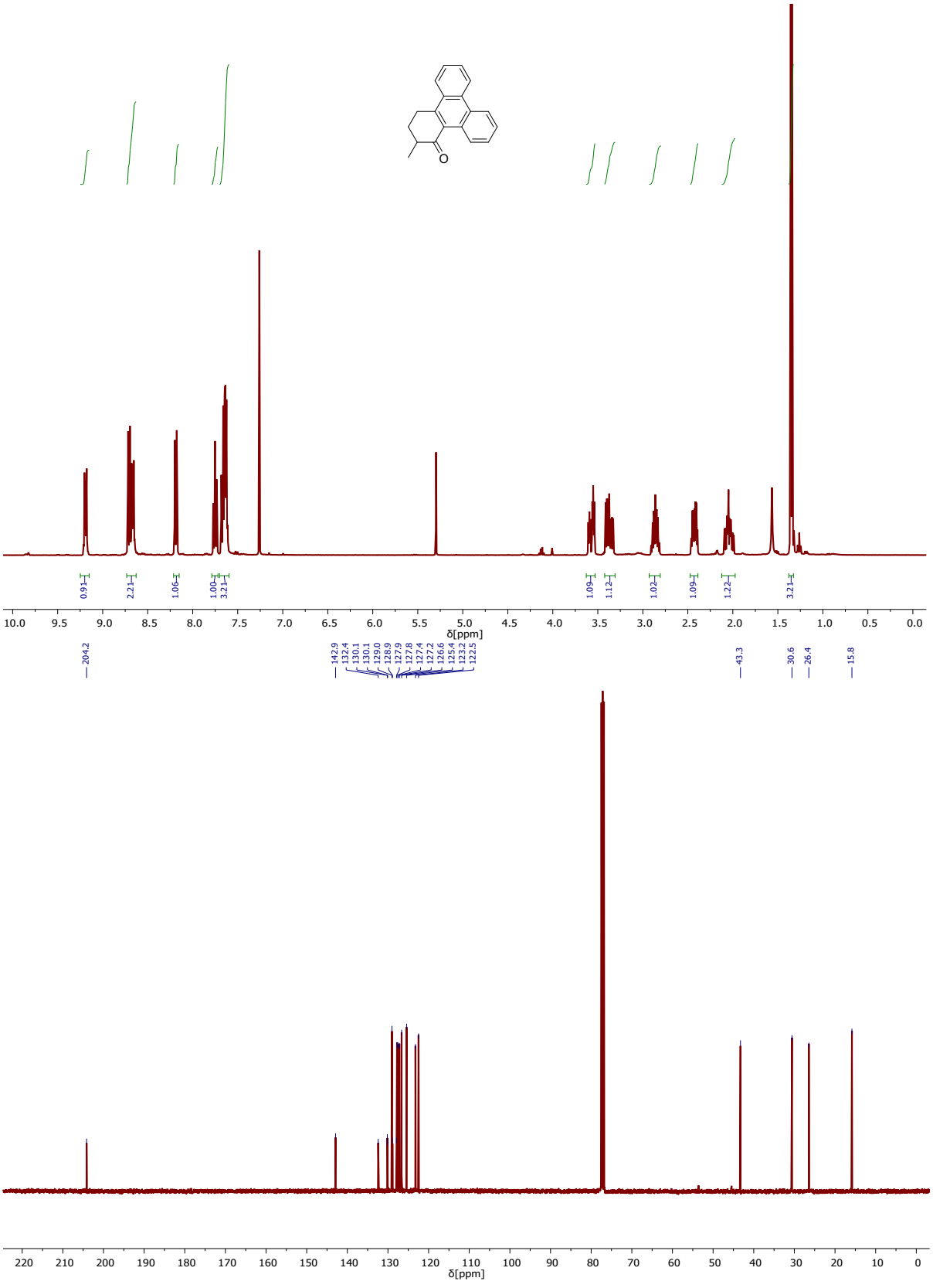
^{1}H NMR and ^{13}C NMR of compound **S8**.



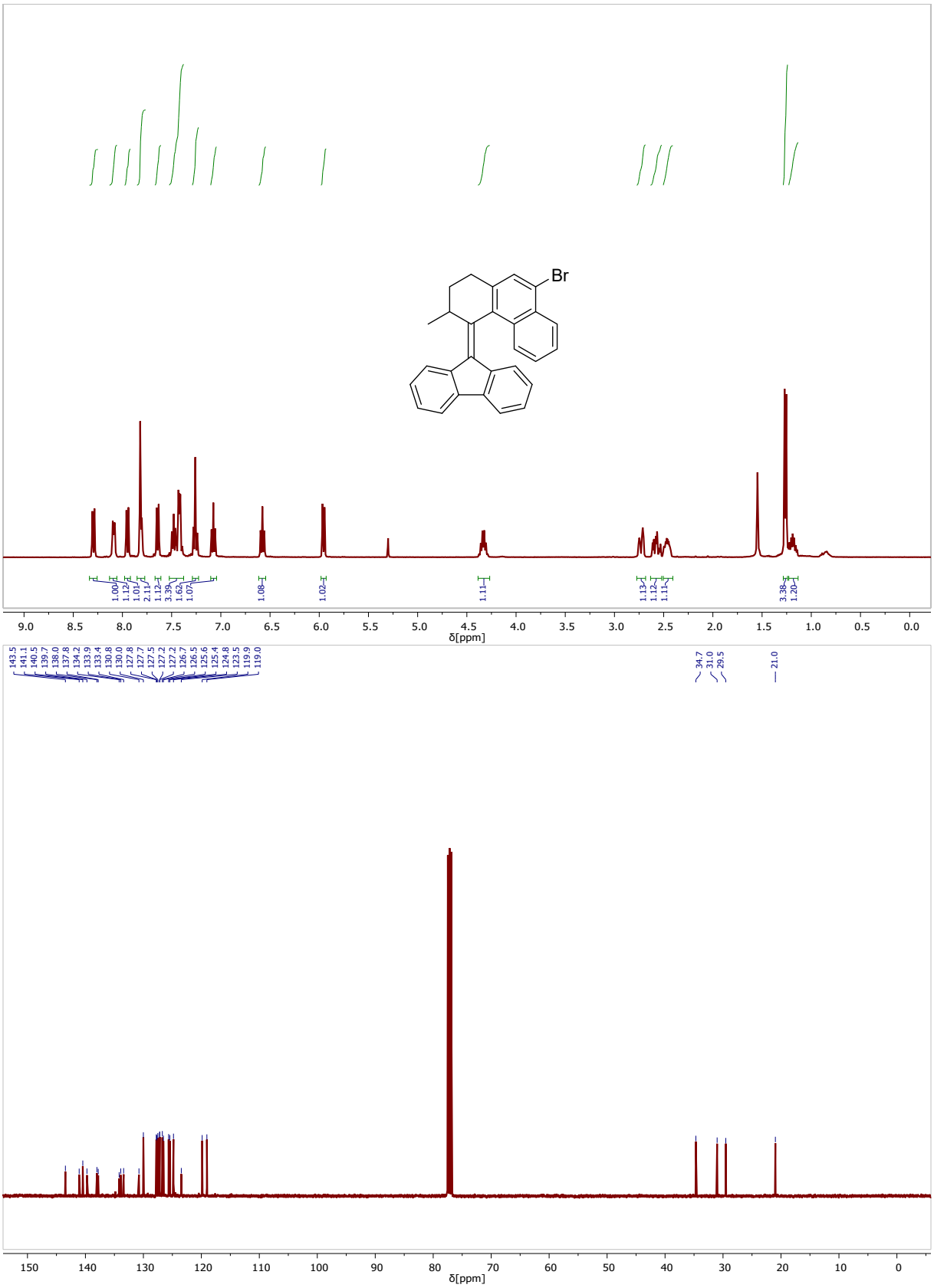
^{1}H NMR of compound **S9**.



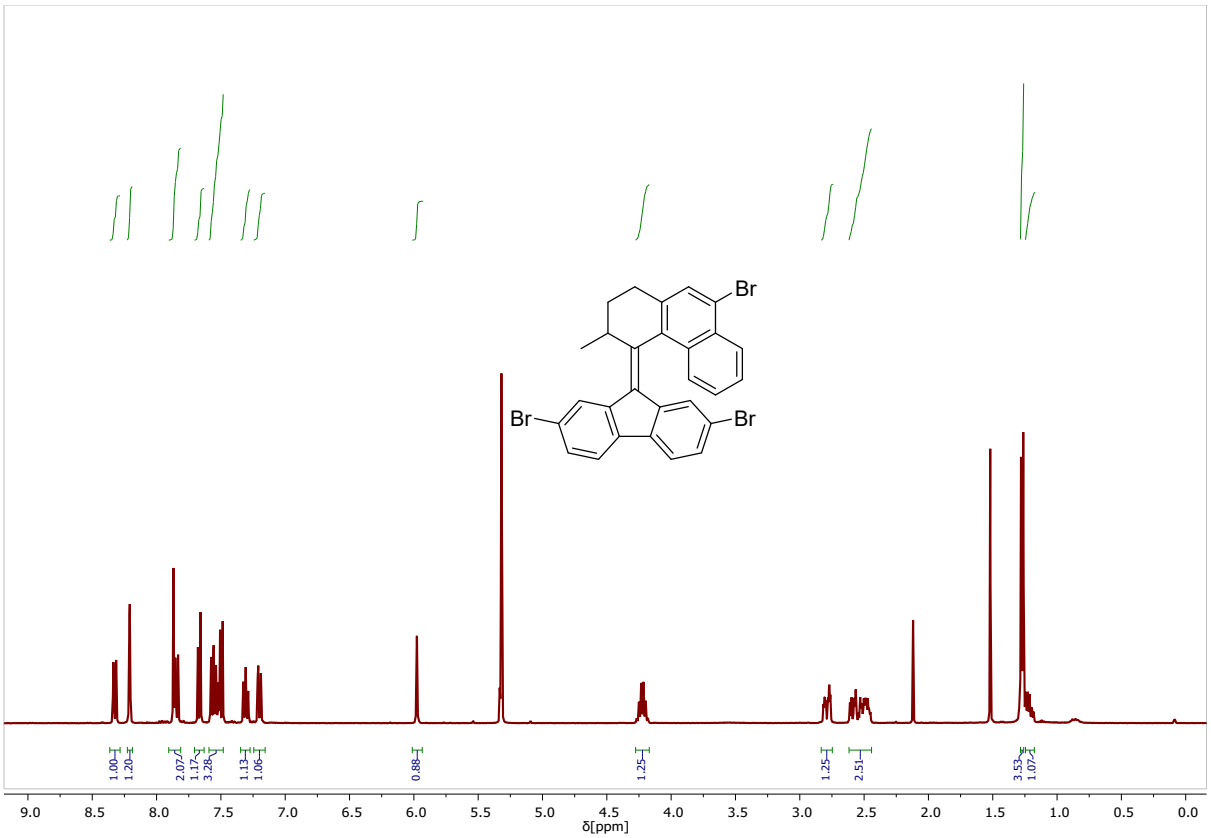
^{1}H NMR of compound **S10**.

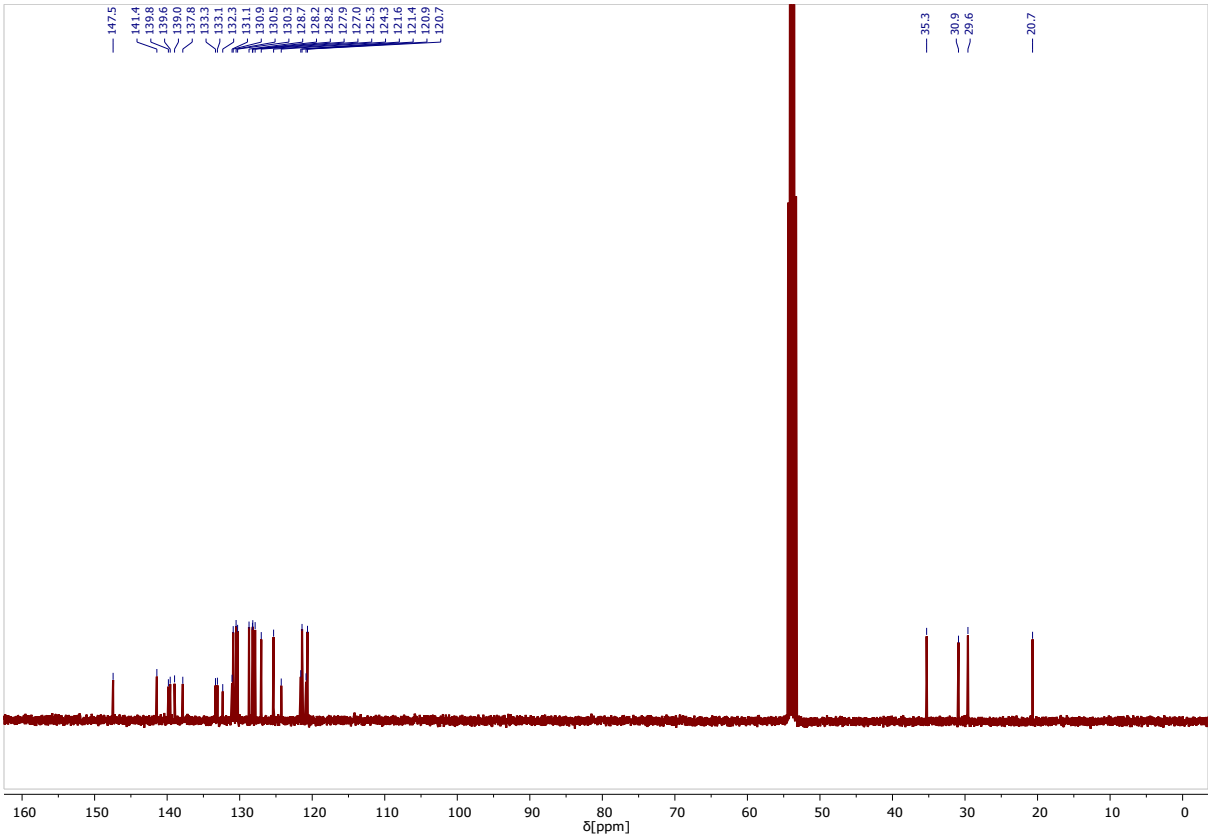


^{1}H NMR and ^{13}C NMR of compound **S11**.

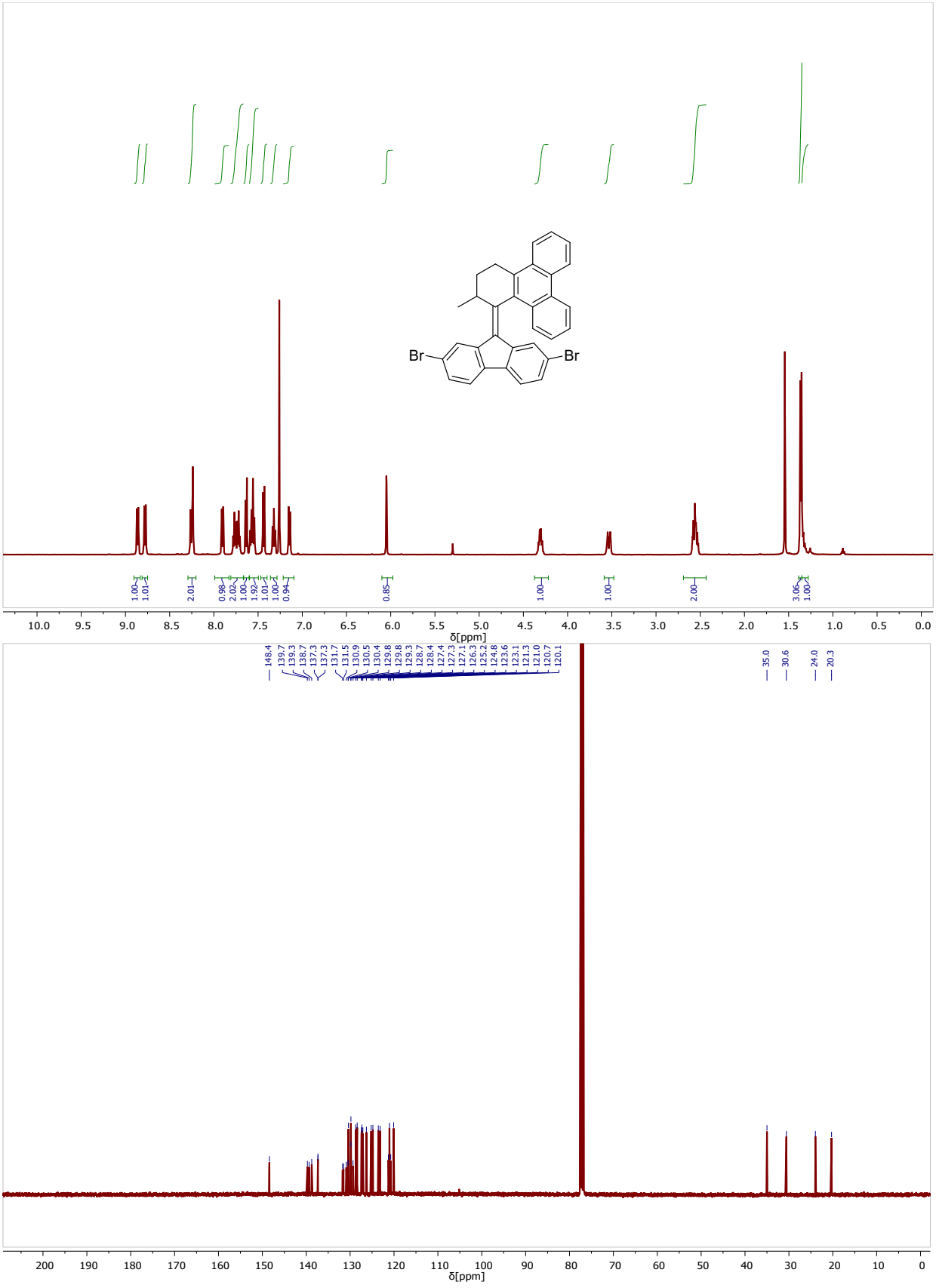


^{1}H NMR and ^{13}C NMR of compound **11**.





^{1}H NMR and ^{13}C NMR of compound **12**.



^{1}H NMR and ^{13}C NMR of compound **13**.

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